PHOSPHORUS DYNAMICS IN BOREAL PODZOLS CONVERTED FROM FOREST TO AGRICULTURE

by

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Abstract

Phosphorus (P) is a non-renewable and vital element for all life and the second most yield-limiting nutrient next to nitrogen in agriculture. The global and regional soil P pools, fluxes and the governing biogeochemistry vary with soil, vegetation, and management types. Limited understanding of the dynamics of P fluxes and pools in the Newfoundland (Nfld) natural and agricultural Podzols hampers decisions on best management options. To fill this knowledge gap, I: (a) assessed the levels and status of P in Nfld farm soils and their relationship with the recommended fertilizer rates across locations and managements; (b) evaluated the utility of ten P-extraction and analysis tests (*P-test*) for P extractability in natural grassland, as well as *forested* and agricultural soils*;* (c) determined P adsorption isotherms for forested and agricultural soil horizons; (d) investigated the P adsorption capacity of long-term managed soils; and (e) carried out a greenhouse trial to evaluate the plant uptake of P from soil layers relevant to soils converted from *forested* to agricultural use.

The provincial Mehlich-3 *P-test* confirmed the relationship between measured P and the recommended P rates, but also suggests possible overfertilization. Soil *P-test* measurements varied with management status and were affected by the soil organic matter (SOM), Al, Fe, and soil depth or horizon. Citric acid extracted significantly more P for all tested soil conditions except for newly converted soils. Phosphorus adsorption capacity varied by soil horizon, depth, and management.

Phosphorus availability and uptake in recently converted soils from *forested* to agriculture varied with soil depth and P sources. Given the variability in results and the possibility for

a mismatch between P application and P uptake for soils, differentially across a range of conversion ages and managements, it is critical that further agronomic work focuses on the detailed understanding of P species and the effect of management on the P biogeochemistry, with a focus on the role of SOM and mineral contents. It is recommended that targeted calibration of *P-test* and recommendations be carried out to cover all sources of variability in soils that have undergone conversion to confirm the relationship between P sources, extractability, and uptake for different conversion and management states.

Keywords: Phosphorus, phosphorus adsorption, soil phosphorus test, phosphorus availability, phosphorus uptake, Newfoundland, Podzol, soil horizon, soil depth.

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Chapter 1. INTRODUCTION AND OVERVIEW

1.1. Thesis Rationale

Phosphorus (P) is a non-renewable resource (Cordell et al., 2009; Cordell & White, 2014; Roberts & Johnston, 2015) and vital element for both plant and animal growth (Mona & Lamberg-Allardt, 2015). Specifically, P is one of the three major crop macronutrients, which, together with nitrogen (N) and potassium (K), govern the capacity of a soil to provide nutrition for a growing plant. The P biogeochemical process in the soil is complex and depends on a complex of environmental factors as affected by soil formation and management. Generally, the inorganic P, i.e., orthophosphate (PO_4), plays a major role in plant growth and productivity, whereas the organic P must be mineralized to inorganic P before plant uptake (Jianbo et al., 2011; Kochian, 2012). The dynamics of soil P in acid soils common in the province of Newfoundland and Labrador (NL) is governed by the unique physicochemical properties of the soil (Ayenew et al., 2018; Debicka et al., 2015; Eriksson et al., 2016; Luo et al., 2017; Read & Campbell, 1981; Roy et al., 2017). Phosphorus availability to plant roots depends on its concentration and solubility, soil pH, the mineral content of the soil, and plant type (Baker, & Eimers, 2015; Eriksson, Gustafsson, & Hesterberg, 2015; Kochian, 2012; Simard et al. 1988).

On the other hand, repetitive and excessive application of P in an agricultural setting to overcome those limitations could lead to an accumulation of P in the soil (Luo et al., 2017) which might not be immediately available to crops but, instead, might be carried by erosion into rivers and lakes, where it acts as a pollutant, a common cause for algal blooms

(eutrophication), and lower water quality (Bailey et al., 2016; Bunting et al., 2016; Malley & Watts, 2016; Schindler et al., 2016). Hence, best management options can only be recommended based on a better understanding of the fluxes and pools of P in the soil. For this, there is a need for a basic understanding of P dynamics and the identification the best way to measure and monitor P in Newfoundland (Nfld) soil conditions.

Most soil tests appropriate for Podzols have only been evaluated in the context of forest nutrition; it is thus important to test the pertinence of these methods in an agricultural context for a meaningful and standardized set of methods on which to base its agricultural management recommendations and each method's potential suitability for inclusion in a locally relevant P index.

Moreover, the province of Newfoundland and Labrador is relatively unique in that most agricultural land, including land dedicated to field crops, has been developed on Podzols. A significant increase in the agricultural output is expected by 2022, a feat dependent on a significant increase in the agricultural land base. This is contingent on the further conversion of forested lands into agriculture. These conversions will bring more Podzols into crop-based agriculture (Government of Newfoundland and Labrador, 2017). Assuming an average fertilization rate of 22 kg P ha^{-1} (Tóth et al., 2014), the total annual input would vary from about 682 metric tonnes per year, for the land currently in agriculture, to 1958 metric tonnes per year, for the planned extent of agricultural lands. This is a significant farm input cost. The hydrologic behaviour of a natural Podzol is distinct from a farmed and tilled Podzol (Altdorff et al., 2017). In agricultural Podzols, infiltration is slower and water retention longer than in natural Podzol, particularly in the newly developed A horizon

above the illuviated Ae horizon. This hydrological behaviour is likely to lead to enhanced surface runoff, erosion, nutrient losses, and limited groundwater recharge under converted soils. Thus, a better understanding of the P dynamics in the local Podzols will contribute to developing sustainable P management.

To my knowledge, this is the first study aimed at understanding the P dynamics in natural, long-term managed, and recently converted Podzols of Nfld.

1.1.1. Thesis Organisation

This thesis consists of seven chapters. Chapter one presents the study rationale, the relationship between chapters, objectives and hypothesis, literature review on the P dynamics in the soil, and boreal Podzol distribution, classification, and properties. Chapters two to six are independent units/manuscripts based on the objectives listed in the next section. Each chapter (two to six) consists of an abstract, introduction, objectives, methods and materials, results and discussion, and conclusion sections. Figure 1. 1 is the schematic conceptual framework adopted from the literatures (Hyland et al., 2005; Jianbo et al., 2011; Sims & Pierzynski, 2005; Bünemann et al, 2010.; Weins, 2002; Ziadi et al., 2013) to show the relationships between chapters two to six. Chapter two addresses the baseline soil test status in the already established Nfld farms, including P index and sorption capacity based on the secondary dataset. Chapter 3 compared the P extractability in natural, recently converted, and long-term-managed Podzols using ten soil P tests (*P-tests*). Chapter four examined the P adsorption isotherm in Podzol horizons of *forested* and *managed* soils. Chapter five determined the P adsorption capacity of long-term managed soil by depth. Chapter six evaluated the P availability and uptake in recently converted forest soils treated

with different P sources in a pot experiment. Chapter seven provided the overall concluding summary of the thesis, which also identifies the research gap.

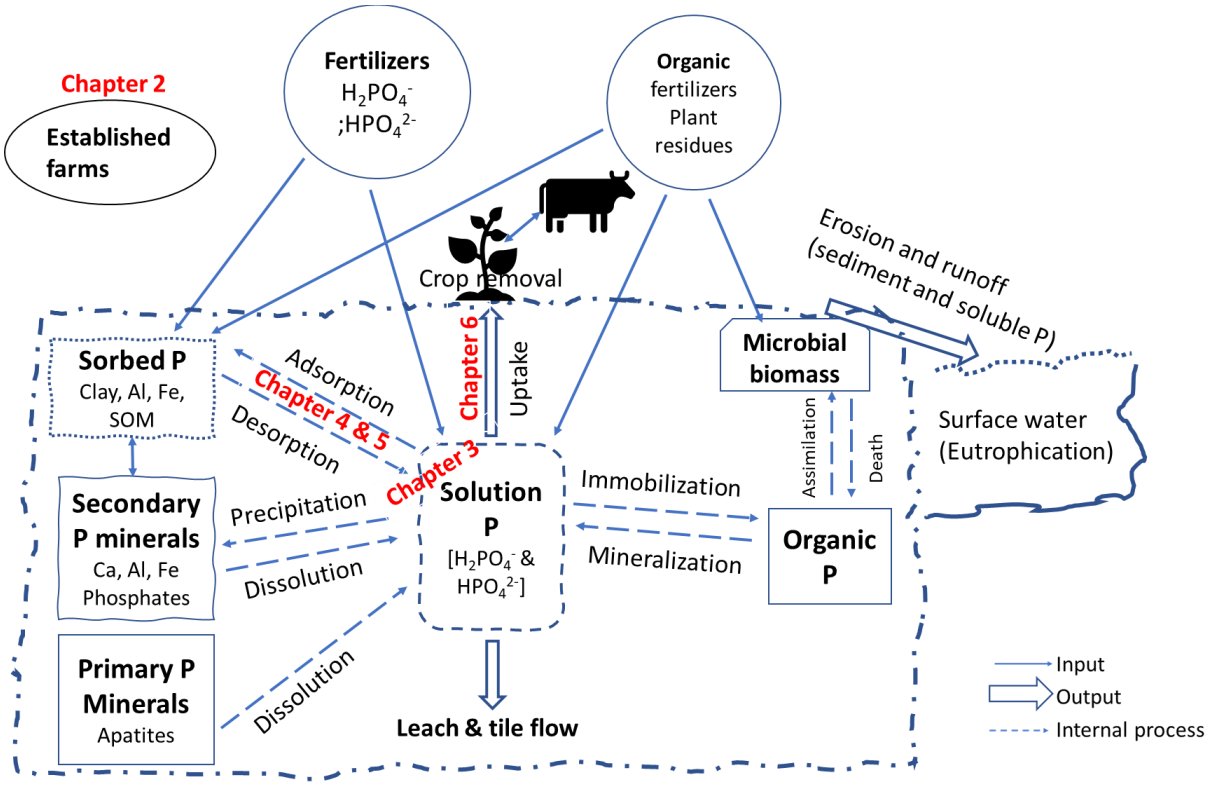

Figure 1. 1. Conceptual framework of P sources and soil phosphorus.

1.1.2. Thesis Objectives and Hypotheses

Chapters two to six address independent objectives targeting specific research problems. As a starting point I surveyed the relationship between farm soil test parameters and lime and nutrient recommendations across Nfld crop types and regions (Chapter 2) and thus identified the distribution of Mehlich-3 P across regions, and crop types with contrasting conditions. Given the likely differences in soil chemical parameters across Podzol soils of various ages from conversion. I hypothesized that P extractability in Nfld surface and subsurface soils is affected by management and location and is dependent on the choice of

P-test (Chapter 3). Further I hypothesized that the P adsorption is dependent on the soil horizons, and that B horizons have higher P adsorption capacity than top LFH, E, AP, and deeper C horizons (Chapter 4). Then I verified the P retention capacity of long-term managed subsurface soils (20-40 cm) versus the top tilled layers (0-20 cm), to verify the conclusions of the previous chapter for agricultural management conditions (Chapter 5). Lastly, I tested the hypothesis that the P availability, as measured by soil P-*test* will depend on the sol depth, and that the measurable plant uptake of P from deeper layers of recently converted Podzols (15-30 cm) was lower than for the top soil layers (0-15 cm); the P availability kinetics was verified by using P in organic or mineral fertilizers (Chapter 6).

1.2. Literature Review

1.2.1. Overview of the P Cycle

Phosphorus is a limited and non-renewable resource that needs attention for economic and environmental purposes (Ulrich & Schnug, 2013). On the other hand, the increasing world population requires more food production, which puts more pressure on the already depleted P rock reserves. Phosphorus production is projected to reach a peak by 2030. Most of the mined proportion of P is used in agriculture sectors (Cordell et al., 2009). Human interference pushes the P cycle in one direction, while the natural P replacement may require ten to a hundred million years. This implies that the geological P cycle has been anthropogenically interrupted; this will have global economic and political consequences. The environmental P cycle, especially the soil P cycle, requires a deep understanding of P sources, pools, sinks and management.

1.2.1.1. P in the geosphere

Phosphate rock in the form of apatite minerals is the major P pool in the earth's crust, which contains about 95% of the mineral P. Apatite has very low solubility; however, small fractions are released to the environment by weathering (Smil, 2000). The largest global (77% or about 50 billion tonnes) phosphate rock reserves are in Morocco and west Saharan Africa. However, China is the leading P producer (Butusov & Jernelöv, 2013). It was reported that about 80% of the mined rocks come from the sedimentary deposit and 75% from a surface mine. Globally about 170 million tonnes of P per year are produced, and China is the largest phosphate rock producer (Butusov & Jernelöv, 2013).

1.2.1.2. Inorganic and organic P in the soil

Between 1850 and 2000, about 550 million tonnes of P, and annually 13-16 million tonnes of P have been applied to the soil, and an estimated 40-50 million tonnes of P accumulated in the soils (Smil, 2000). Once P fertilizer is added to the soil, the available P is either dissolved, and a small amount is available to plant roots, or fixed with sesquioxides compounds, mainly Al, Fe, and Ca (Read & Campbell, 1981), soil organic compounds (Debicka et al., 2015; Eriksson et al., 2016; Read & Campbell, 1981) and poorly crystalline aluminium (Al) and iron (Fe) oxyhydroxides (Ayenew et al., 2018). Also, P is available in clay minerals. The solubility of P in the minerals depends on the soil characteristics such as soil pH. For example, Al-P and Fe-P are less soluble in the lower pH range (acidic soil), while Ca-P is stable at higher pH (alkaline soil) (Eriksson et al., 2015; Kruse et al., 2015). The P forms vary with soil characteristics and various factors such as soil management, climate, and P sources.

The P cycle in the soil depends on the chemical and biological processes such as adsorption and desorption activities, P sources, microbial activities, and soil genesis. Adsorption or fixation is one of the major processes controlling the P cycle in the soil (Lajtha et al., 1999). The dynamics of P in Podzol is not well understood. For example, studies reported contradictory results on the effects of soil pH on P adsorption and mobility in the soil, often in relationship to the range of pH considered. Beaker et al. (2015) reported that pH does not affect the forest soil P sorption (Baker et al., 2015), whereas several studies reported that pH is one of the most important adsorption regulating factors (Grand & Lavkulich, 2013; Grand & Lavkulich, 2015). A long-term P application to the soil increased the inorganic P fixed by Al and Fe (Haygarth et al., 2014) and Ca (Read & Campbell, 1981) via the adsorption process.

Furthermore, the sources of organic P (OP) are mainly plant and microorganisms, which form OP through a biochemical reaction between P and carbon via phosphorylation process (Condron et al., 2005). Also, OP is the form of P mainly attached to organic chemicals such as humus, organophosphate pesticides, and microbial and plant biomass (Imvittaya, 2014). In most soils, the proportion of OP is more than 50% of the total P (Evangelou, 1998) and up to 90 to 95% in high organic soils (with greater than 20-30% organic matter) (Condron et al., 2005; Sims & Pierzynski, 2005; Smil, 2000), and 30 to 65% in mineral soils (Sims & Pierzynski, 2005). The major OP sinks are nucleic acids, phosphate esters, and phospholipids. Some examples of the OP forms are orthophosphate monoesters such as inositol hexakisphosphate (IP6), sugar phosphates, and orthophosphate diesters such as nucleotide phosphate, teichoic acid, aromatic compounds, and phospholipids (Condron et al., 2005; Kruse et al., 2015). Inositol phosphates are the dominant (about 80% of total

organic P) species among the orthophosphate-monoesters (Condron et al., 2005; Sims & Pierzynski, 2005). The capacity of P release from the OP sink is reported as nucleic acids>> phosphate esters> phospholipids. The carbon to P ratio is believed to affect the degradation of organic P species when the ratio of carbon to P is less than 200; the organic compound will breakdown and release P whereas the degradation is negligible when the ratio is greater than 300 (Evangelou, 1998).

Thus, while about 3 to 24% of organic P is stored in the soil microbial biomass (Esbroeck, 2015) this varies with land uses; for example, from 2 to 5% in arable to about 25% in grassland soil microbial biomass (Sims & Pierzynski, 2005). The fraction of OP released from the decay or enzymatic hydrolysis of microbes, which further transforms to plant-available P. Also, the OP released from the microbial biomass could be fixed on the soil surface and subsequently become a source of P (Kruse et al., 2015). Figure 1.2 shows the conceptual model of soil organic P sources, transformation, uptake and loss (Condron et al., 2005).

1.2.2. P Sources

The two major P sources are inorganic P from mineral fertilizer and organic P from organic wastes or plant residues. The P dynamics in the soil partly depends on P sources as reviewed in the following subsections.

1.2.2.1. Organic P

Generally, the amount of total and soluble P in organic fertilizers is lower compared to inorganic fertilizer, except for a few exceptions like pig slurry (Kashem et al., 2003). However, the bioavailability of organic P depends on the biology and chemistry of the soil.

The P concentration in the commonly used organic fertilizers largely varies based on the measurement technique, as presented in Table 1. 1 (Kashem et al., 2003; McLaughlin, 2005). Ajiboye et al. (2007) quantified the P in biosolids, as well as hog, dairy, beef, and poultry manures using sequential extraction followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and 31P nuclear magnetic resonance (NMR) and synchrotron-based P 1s X-ray absorption near-edge structure (XANES) analysis. Most of the total P measured in all organic fertilizers except in poultry was labile P (orthophosphate) in the form of soluble calcium phosphates while calcium phytate was the dominant form of organic P. Also, the recalcitrant Al and Fe phosphates were measured in the biosolids and manures (Ajiboye et al., 2007).

The forms of P in soil treated with organic fertilizer depend on the sources of organic fertilizer, fertilizer application rate, frequency and treatment duration, soil management and soil characteristics (Kashem et al., 2003). Usually, excessive P has been added to the soils from the organic fertilizers to fulfil the crop's nitrogen requirement (Shober, 2006). Kashem et al. (2003) incubated a Lakeland silty clay loam (Gleyed Rego Black Chernozem) soil treated with three types of organic fertilizers (biosolids, hog manure and dairy manure) at three doses (123, 307 and 614 mg P kg^{-1}) for 1, 4, and 16 weeks. They found that the labile P (H_2O-P and $NaHCO_3$-P) in the soil amended with fertilizer > hog manure > cattle manure > biosolids while the non-labile or recalcitrant P (HCl-P, NaOH-P and residual-P) was inconsistent after incubated for 16 weeks due to biochemical transformations (Kashem et al., 2003). The same group of researchers studied the impact of these organic fertilizers on extractable P of two types from amended alkaline soils

(Gleysolic Humic Vertisol and Gleyed Rego Black Chernozem). They reported comparable responses in both studies. However, Karem et al. (2004) reported that the order of P extractability in the soil treated with organic fertilizers as Mehlich-3 > Kelowna > $NaHCO_3$ > NH_4Cl > H_2O. The P extractability is affected by soil types, fertilizer types, application rate, and incubation time (Kashem et al., 2004). Thus, the amount of P, and its extractability in different soil types treated with different organic fertilizers is highly varied and requires monitoring for agronomic and environmental purposes.

Table 1. 1. P concentration in common organic fertilizers.

Available or **total P**	**Biosolids**	**Hog manure**	**Dairy manure**	**Poultry manure**	**References**
H_2O-P, mmol P kg^{-1} dry weight	65.00	388.00	36.00	-	(Ajiboye et al., 2008)
	0.30	9.90	2.40	5.20	(Ajiboye et al., 2007)
Total P, g kg^{-1} dry weight	17.20	33.40	5.50	-	(Ajiboye et al., 2008)
	12.60	39.80	13.20	14.30	(Ajiboye et al., 2007)
	1.70	3.33	0.55	5.00	(Kashem et al., 2004)

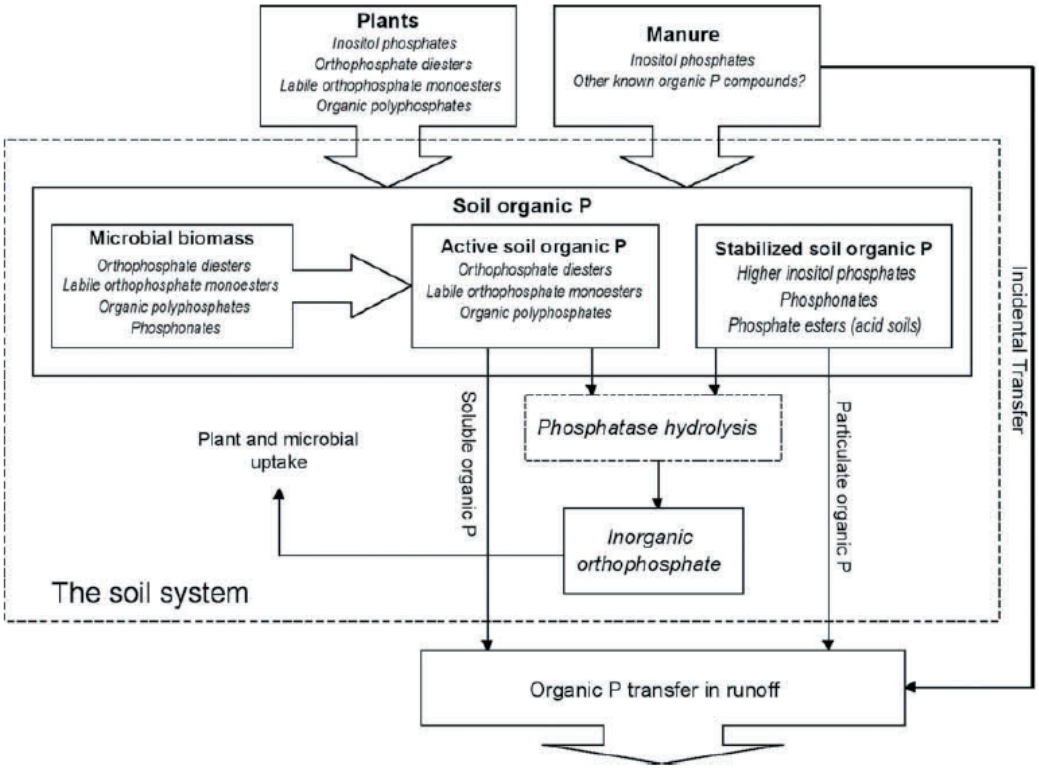

Figure 1.2. Conceptual model of organic P transformation in the soil (Condron et al., 2005).

1.2.2.2. Inorganic P

All mineral P fertilizers are sourced from phosphate rock (mainly sedimentary rock). The mined P rocks are further processed and either mixed with other nutrient additives or used as fertilizer without additives. The common sources of inorganic P are superphosphate, ammoniated phosphates, and compound phosphates. They have different chemical compositions. Ammoniated phosphates (monoammonium phosphate (MAP) and diammonium phosphate (DAP)) are the most widely used fertilizers due to the two-fold nutrient stream, i.e., N and P, whereas the global use of superphosphates is declining due to the degraded quality of phosphate ores. Inorganic P fertilizers are expected to provide maximum soluble P (PO_4^{3-}) concentration in the saturated soils. Table 1. 2 shows the

relative orthophosphate fractions and solubility of different P fertilizers (McLaughlin, 2005).

Most of the inorganic fertilizers presented in Table 1. 2 are readily soluble. Nevertheless, the clay and sesquioxide minerals fix highest fraction of dissolved orthophosphate and form more stable P species. Karem et al. (2003 and 2004) compared the amount of labile P in soil treated with monoammonium phosphate (MAP) and organic fertilizers. In both experiments, soils amended with MAP provided higher labile P (H_2O-P and $NaHCO_3$-P) concentrations. Also, P transformation in hog manure is similar with MAP fertilizer (Kashem et al., 2003, 2004). However, the formation of P species (labile or recalcitrant P) depends on the soil types, application rates, and incubation time (Kashem et al., 2004).

Table 1. 2. Phosphate fertilizers and P concentration of their saturated solutions (McLaughlin, 2005).

Phosphorus fertilizers	[P], mol L^{-1}
Monocalcium phosphate	4.0-4.5
Monoammonium phosphate	2.9
Monopotassium phosphate	1.7
Triammonium pyrophosphate	6.9
Diammonium phosphate	3.8
Dipotassium phosphate	6.1
Dicalcium phosphate	2.0×10^{-3}
Hydroxyapatite	1.0×10^{-5}

1.2.3. P Sinks and Losses

1.2.3.1. P sinks

The stability of P in the soil depends on P sources and forms, environmental conditions, interaction within and among the soil, crop types, and level of microbial activities. The P sources added to the soil transform to different P pools such as available P, occluded P on the surface of clay, and adsorbed by metal oxides. Generally, the equilibrium kinetics between dissolution-precipitation, desorption-adsorption, mineralisation-immobilisation, and organic-inorganic determine the stability of P in the soil. Most of the dissolved P is reabsorbed by the soil, whereas only 15-30% is utilized by the plant roots (McLaughlin, 2005). In particular, P bound to minerals like Al and Fe and organic matter is more stable than Ca-bound or apatite, which is easily affected by weathering (Figure 1.3). Also, the P bound to humic acid is resistant to microbial mineralization (Sims & Pierzynski, 2005). Above all, understanding the formation of P as exhibited in Figure 1.3 might help to conceptualize management of soil P for both economic and environmental benefits.

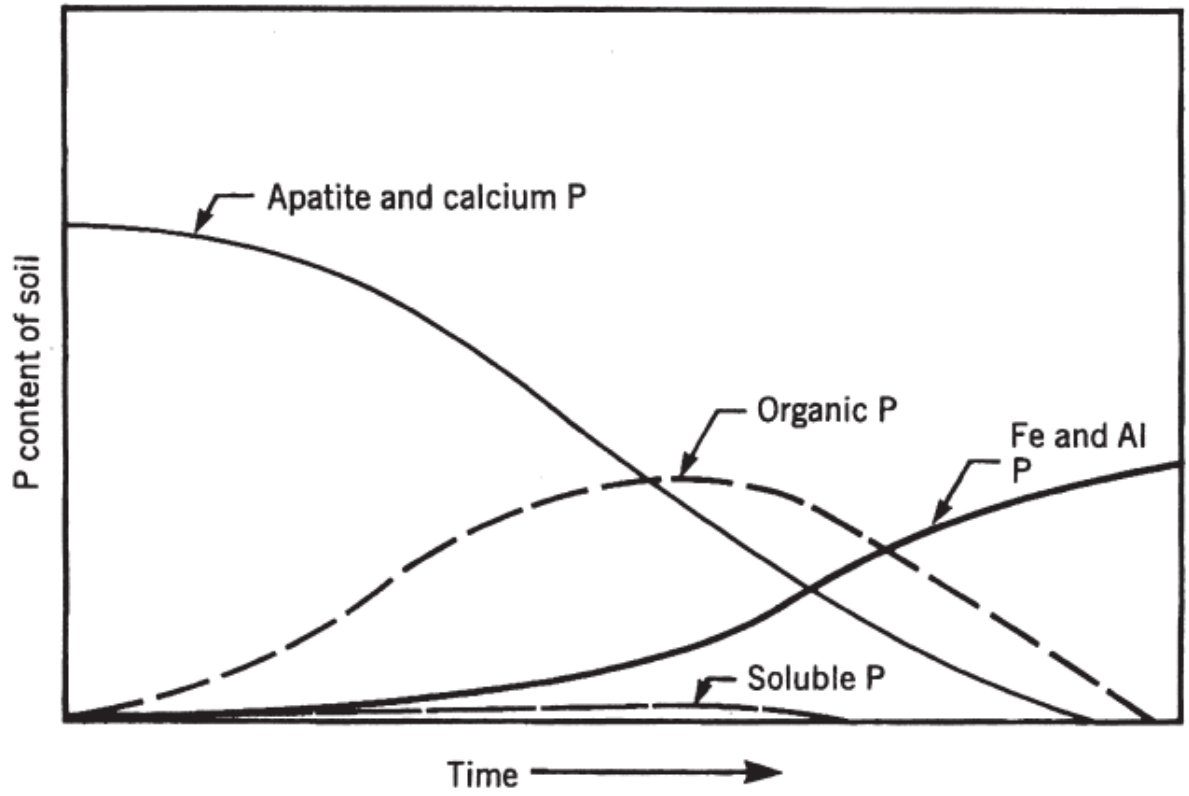

Figure 1.3. Relative distribution of the major forms of soil P during soil development as related to time (Sims & Pierzynski, 2005).

1.2.3.2. P losses

Agriculture runoff (Eriksson et al., 2015; Hart et al., 2004) and wastewater discharge (Smil, 2000) are the major sources of P transfer to the water bodies. Also, the P in the soil can be transported via suspended particle, colloidal, and dissolved form to water bodies (Liu et al., 2014). As mentioned elsewhere, because of the attributes of P, its loss due to drainage is minimal, but more P is lost along with the soil particle in the runoff (Weiner, 2007). Also, Carefoot and Whalen (2003) confirmed that the P loss via soil particulates (Carefoot & Whalen, 2003).

Additionally, the hydrolysis and organic P mineralization are other mechanisms involved in P release from the soils. Soils received organic fertilizer contribute to a large proportion of P loss (Fuentes et al., 2006). Excessive use of organic fertilizers such as biosolids, and dairy and hog manures might increase the loss of P to the environment (Kashem et al., 2003, 2004). Moreover, the P loss is affected by the soil type and management including frequency, sources and methods of P application, the rate of P applied, tillage, land cover, season and topography (Andraski et al., 2003; Daverede et al., 2003; Oelmann et al., 2011; Qian et al., 2004; Radcliffe & Cabrera, 2007).

Furthermore, a higher total P loss was detected in agriculture drainage (Carefoot & Whalen, 2003; Williams et al., 2016), and runoff sediments (Daverede et al., 2003), which are affected by land use and soil management types. Andraski, et al. (2003) reported that the P loss from no-tilled soil with a history of manure application and high soil P level was less than a tilled soil without a history of manure application. A no-tilled soil shows increased permeation and less sediment loss due to plant residue cover. As a result, a no-tilled soil reduced an averaged 57% of dissolved P, 70% of bioavailable P, and 91% total P loss in the runoff when compared to tilled loamy soil (Andraski et al., 2003). Contrariwise, Daverede et al. (2003) reported a higher loss of bioavailable, dissolved, and total P in no-tilled soil compared to tilled soil. However, greater sediment load was measured in tilled plots, and little difference of time to runoff and runoff volume was reported during the spring rain simulation (Daverede et al., 2003). Also, a three decade (1985-2016) meta-analysis compared the particulate and dissolved P losses from no-till and conventional tillage farms. The study found that no-tilled treatment has 45-55% less loss of particulate

P than tilled farms, but the loss of dissolved P increased (Daryanto et al., 2017), whereas Williams et al. (2016) reported that tillage reduced the P concentration and loads in the tile drainage compared to no-tilled field (Williams et al., 2016). The increased soil organic matter has been able to decrease P loss (Daryanto et al., 2017), which might retain mobile P. Overall, the effect of tillage on the P loss was inconsistent.

A laboratory-based P leaching experiment in three types of soils found that 97% of P was leached from the A_2 horizon of Podzol (Hanna, 1966). However, this might vary in the field experiments. The adsorption/desorption of P in Podzol under cold climate regions like Newfoundland and Labrador is yet not studied and needs to be addressed to have a better understanding of P dynamics.

1.2.4. Soil Properties Affecting P Availability, Adsorption/Desorption, and Uptake

1.2.4.1. Cation Exchange Capacity and Soil Cations

The soil adsorption, transformation, and release of P to the soil solution and water is mainly controlled by the electrochemical surface of the silicates, oxides, and organic matter (Evangelou, 1998). Cation Exchange Capacity (CEC) is an important variable for soil chemistry, soil fertility, soil management, nutrient movement, and availability. The major cations adsorbed on the surface of the soil are Na^+, K^+, Ca^{2+}, Mg^{2+}, and Al^{3+} depending on the pH, colloid, organic, and clay content of the soil. The major soil colloids responsible for exchange reactions are sesquioxides (clay with oxides of Al and Fe), organic (fluvic and humic acids), chlorite, smectite, kaolinite, and amorphous and paracrystalline clays. The cations electrostatically interact with the negatively charged surface of these colloids.

When the soil pH < 6, Al^{3+} is the dominant exchangeable cation, and at pH>7, Ca^{2+} is the dominant cation followed by Mg^{2+} (Essington, 2004; Read & Campbell, 1981; Tan, 2005). The CEC of mineral soils depends on the content of phyllosilicates and hydrous metal oxides (Essington, 2004). Soil with high clay content adsorbs more P due to its large surface area and the presence of sesquioxides on the clay surface. The CEC analysis of 10 mineral soils indicated that Vertisols have the highest CEC (50.1 ± 16.6 $cmol_c\ kg^{-1}$, n= 80) followed by Andisols (30.9 ± 18.4 $cmol_c\ kg^{-1}$, n=35). The CEC of Podzols was 26.7 ± 30.1 $cmol_c\ kg^{-1}$, which is almost half of Vertisols' (Essington, 2004). Moreover, the CEC of a given soil affects the chemical methods used to extract P in the soil (Kuo, 1996). Also, the level of CEC used to calculate the amount of the limestone required to raise the soil pH. Hence, CEC is one of the important parameters to understand the soil P chemistry.

1.2.4.2. Metal-humic Compounds

This subsection emphasizes the roles of organometallic complexes (mainly humic and fulvic acids related) in the soil P dynamics. The soil organic matter (SOM) has been recognised as the major influential factor in the biogeochemical soil process in general and for specific nutrients like P and N. The greater fraction of decomposed organic matter is humus, which accounts for 50-85%, and the rest (15-50%) are non-humic substances (Tan, 2005). The humic substances are characterized as hydrophilic, reactive, negatively charged, and labile. The functional groups responsible for metal-humic complex formation are carboxyls (COOH), hydroxyls (OH), and carbonyls (C=O). The adsorption of metals on the humic-clay surface depends on the "ionic strength, pH, type of clay minerals, type of functional groups, and type of competing cations" (Evangelou, 1998). The pH and

competing cations drive the interactions of the metal-humic complexes. These interactions could be electrostatic (Coulombic), inner-sphere complexation (chelation), and weak water bridging. The organic material is reported to affect the CEC of the soil which varies from 36 $cmol_c.kg^{-1}$ at pH 2.5 to 213 $cmol_c.kg^{-1}$ at pH 8 (Evangelou, 1998). Metal-humic complexes with a positively charged surface have tends to adsorb negatively charged orthophosphates and other anions from the soil solution. The P agglomerates with the metal-humic complex and forms a nonhydrolyzable humic-metal-orthophosphate, which could affect the determination of organic P (Condron et al., 2005; Liu et al., 2014). Schnitzer and Desjardins (1969) characterized the leachate collected in a lysimeter placed between the Ae and Bhf horizons and reported about 87% fulvic acid in dry ash-free leachate (Schnitzer & Desjardins, 1969). This technique could serve as a proxy for soil organic content, which might provide information on the interaction and types of organic P. However, they did not measure the soil organic content. Under favourable soil conditions, the organic P complex might decompose or desorb and contributes to available P.

1.2.4.3. Soil pH

The formation of P species depends on the soil environmental conditions and soil characteristics. Soil pH is the other important factor controlling the formation of P species. For example, the equilibrium of aqueous phosphate in Equation 1-1 and Figure 1.4 shifts left when pH decreases and shifts right as pH increases (Weiner, 2007). Also, Figure 1.4 shows that H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, and PO_3^{-4} are dominant phosphate species at pH <2, pH 2-7, pH 7-12, and pH>12, respectively. Although the optimum P availability occurs

between pH 6 and 7, P loss may also occur in this range. Additionally, Sims and Pierzynski (2005) reported that $H_2PO_4^-$ and HPO_4^{-2} are the dominant species between pH 4.0-5.5 and pH>8, respectively (Sims & Pierzynski, 2005). In field soil, less than 1% (<1 kg ha^{-1}) of the total P is available in the soil solution (Sims & Pierzynski, 2005). The chemical formation and equilibrium between labile and nonlabile P species depend on the soil pH and P solubility. Furthermore, Figure 1.5 shows the non-labile Al-P and Fe-P are species dominant in the acidic pH range, while Ca-P species are dominant at alkaline pH ranges (Weiner, 2007). Figure 1.6 shows the solubility of these P species based on the soil pH (Evangelou, 1998). However, almost it is impossible to attain a state of equilibrium in the actual soil environment.

The pH is the key soil parameter governing P species. The acidic soils having with lower pH are dominated by phosphate adsorbed on the Al and Fe oxides, as shown in Figure 1.7 (Eriksson et al., 2015; Jones, 2001). For example, the red acidic soils of Qiyang, China are dominated by Al-P and Fe-P (Luo et al., 2017).

On the other hand, there are contradicting reports on the effect of soil pH on the P adsorption and mobility (Baker et al., 2015; Gustafsson et al., 2012; Read & Campbell, 1981). The P mobility decreased as the acidity increased due to the adsorption of P by Al and Fe (Baker et al., 2015), which reduces the P uptake by the plant (Chen et al., 2016). For example, the concentration of total P in the humus and mineral soils of the Avalon Peninsula was found to be 3.6 meq $100g^{-1}$ and 226 meq $100g^{-1,}$ respectively, while 2.6 meq $100g^{-1}$ and 1.5 meq $100g^{-1}$ was found in the humus and mineral soils of Western Newfoundland forest, respectively (Page, 1971).

$$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+ \leftrightarrow HPO_4^{2-} + 2H^+ \leftrightarrow PO_4^{3-} + 3H^+$$ Equation 1-1 (Weiner, 2007)

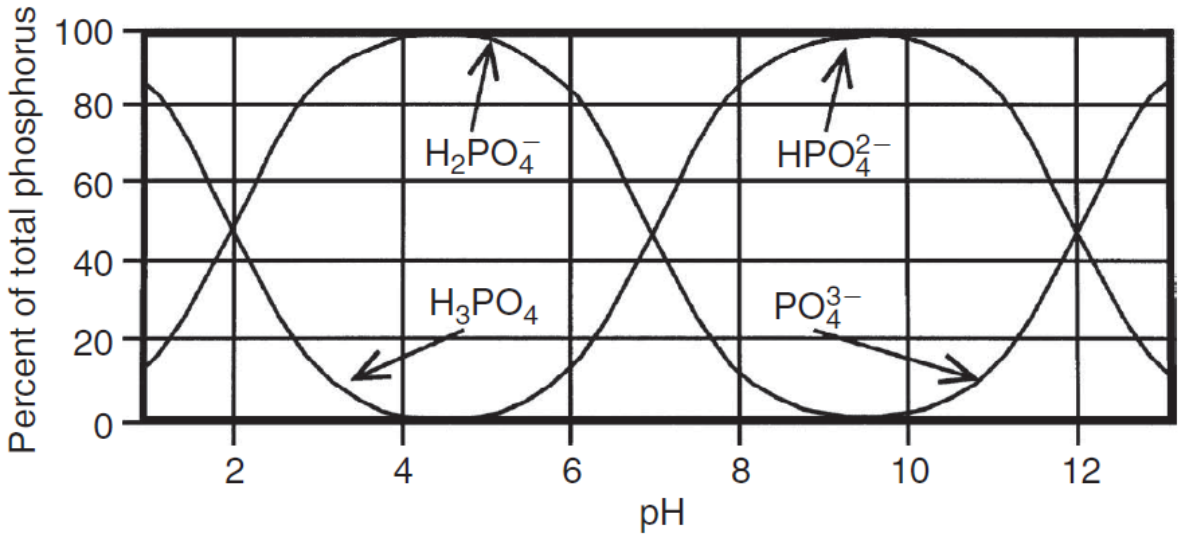

Figure 1.4. pH dependence of dissolved phosphate species equilibrium (Weiner, 2007).

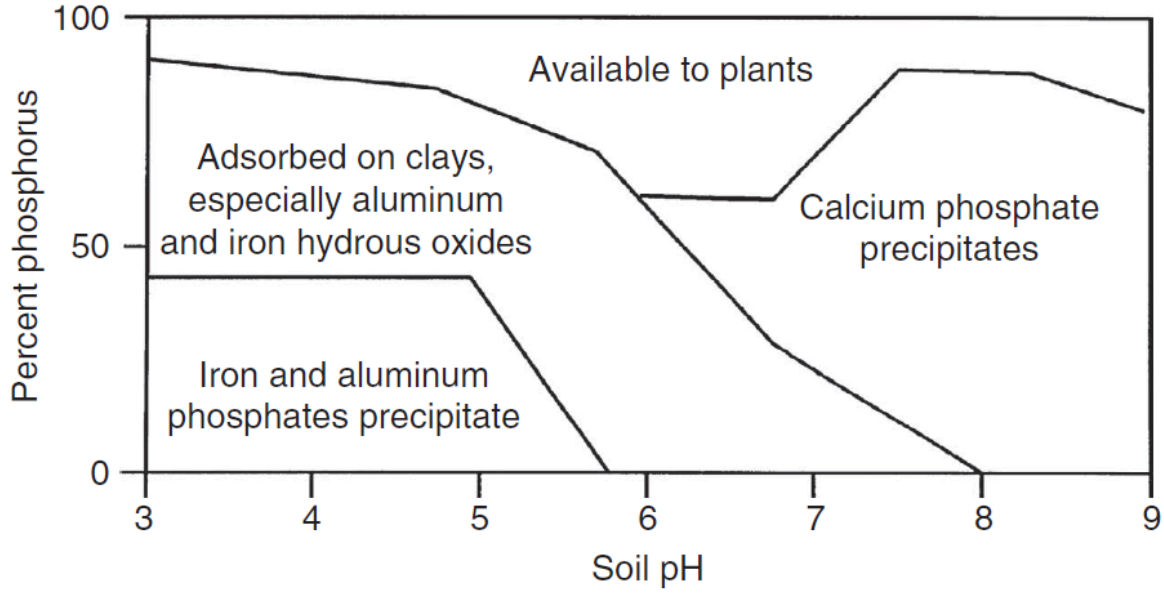

Figure 1.5. Forms of immobile phosphorus (Weiner, 2007).

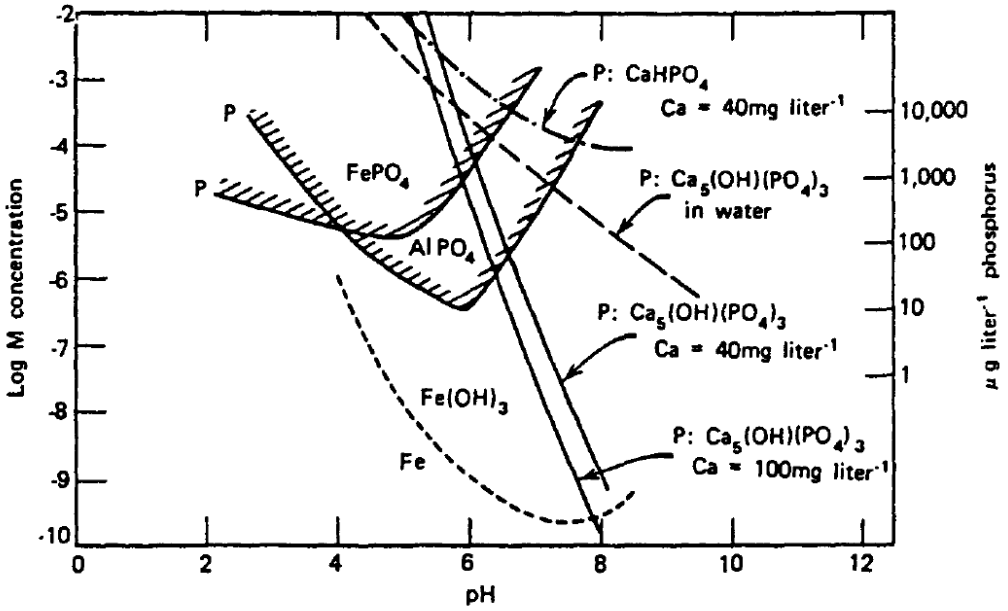

Figure 1.6. Influence of pH on the solubility of various P species (Evangelou, 1998).

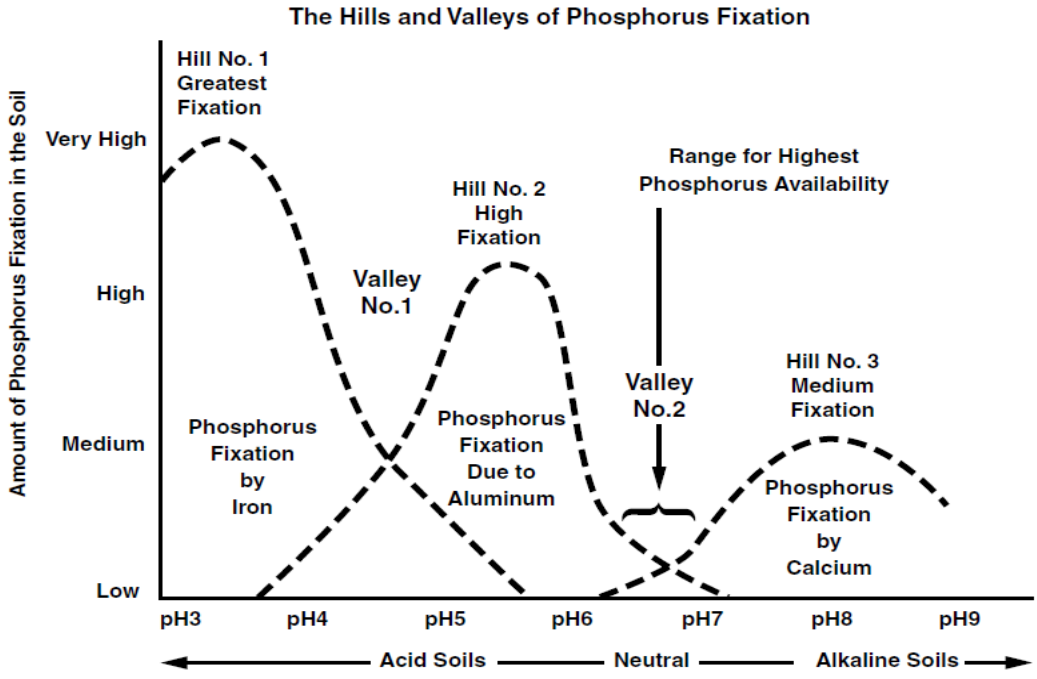

Figure 1.7. The formation of P compound in the soil depends on the soil pH (Jones, 2001).

1.2.4.4. Soil Redox Potential

Soil has a wide range of redox potential (Eh) (-300 to +900mV) also affected by the type of management. The availability of P in the soil is indirectly affected by Eh through its relationship with the solubility of the metals (Husson, 2013). The degradation of organic matter is faster under aerobic conditions and very slow under anaerobic conditions, which affects the formation of humic compounds and, consequently, affects the formation of organic P and organic-metal-P complexes. For example, under anaerobic or reducing conditions, the iron is reduced, and the P is released to the soil or not precipitated with iron, which increases P availability and mobility (Haggard et al., 2004).

1.2.4.5. Soil microbes

The soil microbes, mainly in the mycorrhizal root zone, help to provide available P by decomposing the organic matter containing P as a source of energy. They play a significant role in the P cycle by transforming unavailable P to available P and vice versa. For example, they help to release orthophosphate from insoluble calcium phosphate, and organic phosphate in the plant and animal tissue. Upon their death, some fraction of organic P in the microbial biomass is available to plants (Weiner, 2007).

1.2.4.6. Effect of Tillage

During the conversion of forest land to agriculture, soil preparation like root removal and initial tilling lead to the mixing of LFH, Ae and B(f/h) podzolic horizons. Eventually, tillage and long-term cropping forms a top plough layer (Ap) that starts as a mixture of LFH and Ae. Because the LFH layer is commonly lost during conversion to agriculture, the plough layer may be significantly constituted of Ae material and essentially devoid of

nutrients and weatherable minerals. The plough layer may also reach into the illuvial horizon, i.e. B horizon. Mixing of this Bf/Bh material bearing large amounts of poorly crystalline oxides into the topsoil could sequester yet more nutrients (especially P) away from the bioavailable pools and have important consequences for agricultural productivity. The impact of tillage on the P species has been studied with inconsistent conclusions (Pierzynski et al., 2005). Conversely, tillage might help in the mineralization of organic P (Holanda et al., 1998). Yet, at present, inconsistent information is available on the distribution of nutrient elements in cultivated Podzol profiles.

1.2.4.7. Effect of Cropping System

Crop rotation has been in practice for a long time and is known to have tremendous benefits on soil management as opposed to monoculture systems due to better nutrient budgeting. The crop rotation mainly helps to improve soil fertility by providing more organic matter to the soil. The organic matter, mainly humic, helps to retain the P as organic species and slowly release plant-available P. On the other hand, the organic matter could fix most of the available P and affect the crop yield (Rheinheimer et al., 2019).

1.2.5. Boreal Podzols

1.2.5.1. Overview of Global Podzols

Globally, Podzols covers about 485 million hectares located in the temperate and boreal regions (Driessen et al., 2000); Canadian Podzols alone covers about 140 million hectares (~15.6%) of Canada's land, which accounts for ~29% of the global Podzols coverage. Also,

this type of soil is estimated to cover about 10 million hectares in some tropical regions of South America and Australia (IUSS Working Group WRB, 2015). The Podzols found in different regions of the world have some similarities and differences in their formation as well as its physical, chemical, and biological characteristics. Most podzolic soils are known to have low fertility, high acidity, to accumulate of organic matter, Fe, Al, and variable water-holding capacity (IUSS Working Group WRB, 2015; Sanborn et al., 2011; Simard et al., 1988). As a result of increased soil acidity and precipitation, the elements like P, K, molybdenum (Mo), and magnesium (Mg) leach from the eluvial surface to the illuvial B horizon; the levels of manganese (Mn) and Al increase to harmful levels in the eluvial layer (Degórski, 2007). The illuvial horizon of Podzols has high organic matter, and is sandy, and acidic (Agriculture and Agri-Food Canada, 2018; Grand & Lavkulich, 2013; IUSS Working Group WRB, 2015; Sanborn et al., 2011). In contrast, the illuvial horizons, i.e., about 10 cm of B horizon, which have an elevated level of clay and organic matter resting under the eluvial horizon, were the source of aluminum (Al) and iron (Fe) leaked.

1.2.5.2. Podzol Classification of Canada

Canada's Podzols are classified into humic, humo-ferric, and ferro-humic based on the iron and organic carbon compositions in the B horizon, the intensity of annual precipitation, and geographical landscape. The humic and humo-ferric soils have high organic content. Humic Podzol is predominant in lowland areas and locations with high annual mean precipitation (i.e. 1500mm to 3000mm), with B horizon having a high content of organic carbon relative to iron. The natural Podzol of western Newfoundland was found to have high organic matter (Schnitzer & Desjardins, 1969).

Humo-ferric Podzol is the most common Podzol group in Canada, which accounts for 65% of the Podzols in the four Atlantic provinces. Also, ferro-humic Podzol commonly occurs in very humid climate areas like Newfoundland, New Brunswick, southern Quebec, and the coastal area of British Colombia. It has a minimum of 5% organic carbon and about 2% Al and Fe complexes. Ferro-humic accounted for 55.8% of the Newfoundland Podzols. The geographical distribution and characteristics of the Podzol groups available in Canada are presented in Figure 1.8 and Table 1. 3., respectively (Agriculture and Agri-Food Canada, 2018). Furthermore, Canada's Podzols are classified into 25 subgroups based on the soil profile characteristics of each great group, such as the presence of the cemented layers and state of transitions to other orders (Sanborn et al., 2011).

1.2.5.3. Podzol Characteristics

The properties Podzol vary based on the regional environmental factors and soil formation materials. For example, the Podzol of Fort McMurray, Alberta, has higher base saturation and pH than other Podzols. Also, the B horizon has higher clay than A horizon when compared to parent materials. The mineralogical analysis of the same Podzol exhibited the following weathering sequences: feldspars > quartz; chlorite > biotite > muscovite, hematite > hornblende > garnet ≥ magnetite. Furthermore, the X-ray diffraction examinations of A and C horizon minerals revealed that the illite, montmorillonite-illite mixed layering, montmorillonite, and kaolinite are the main species (Pawluk, 1960).

The podzolic B horizon has a high pH-dependent cation exchange capacity (CEC), less than 50% base saturation, high water holding capacity (uncemented soil), high capacity to fix phosphate, and contains more clay than the overlaying horizon (Agriculture and Agri-

Food Canada, 2018). However, Grand and Lavkulich (2013) reported a negative correlation between pH and effective CEC in the natural illuvial soil of western Canada, which might be related to the formation of an organic-Al compound (Grand & Lavkulich, 2013).

Table 1. 3. Classification criteria for the Canadian podzol B horizons soil (Agriculture and Agri-Food Canada, 2018).

Features	Humic Podzol	Ferro-Humic Podzol	Humo-Ferric Podzol
B Horizon	Bh > 10 cm thick	Bhf > 10 cm thick	Bf, or thin Bhf + Bf, > 10 cm thick
Organic C	>1%	>5%	= 0.5-5%
Other	pyrophosphate Fe < 0.3%, Organic C/pyrophosphate Fe ≥ 20	pyrophosphate Al+Fe ≥0.6% (≥0.4% for sands)	pyrophosphate Al+Fe ≥0.6% (≥0.4% for sands)

Table 1. 4. Taxonomic correlation of the Canadian soil order and great group with US and FAO classification systems (Canadian Agricultural Services Coordinating Committee, 1998).

Canadian System	**U.S. Soil Taxonomy**	**FAO System**
Podzolic	Spodosols, some Inceptisols	Podzol
Humic Podzol	Cryaquods, Humods	Humic Podzol
Ferro-Humic Podzol	Humic Cryorthods, Humic Haplorthods	Orthic Podzol
Humo-Ferric Podzol	Cryorthods, Haplorthods	Orthic Podzol

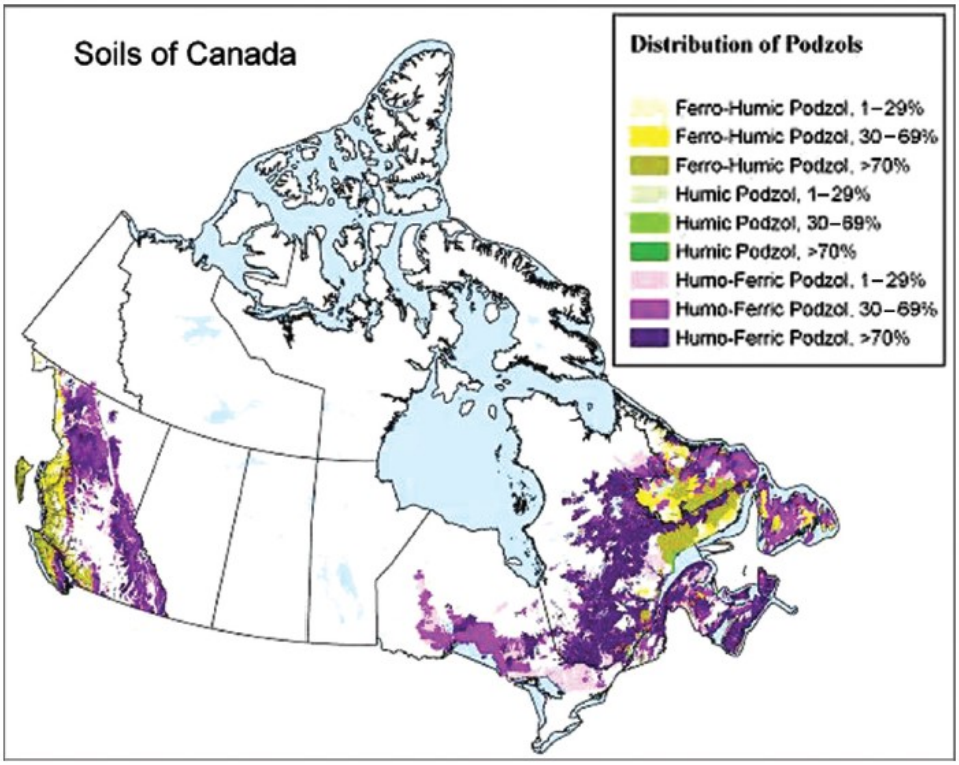

Figure 1.8. Distribution of Podzol great groups in Canada. Source: (Sanborn et al., 2011).

1.2.6. Soil P Tests

The extraction of soil P requires an understanding of regional soil chemistry for selecting the most locally relevant chemical extraction methods. Extraction methods could be either single extractions or sequential fractionation methods to measure P in different pools. In most cases, diluted acids and bases are widely used to extract different P forms in different soil types, mainly based on the soil properties, specifically soil pH (Jones, 2001). The P extraction mechanisms in the soil involve solubilizing, desorbing, complexing, and replacing of anions (Elrashidi, 2010). The acid extractants targeted to dissolve Al and Fe bound P while the Ca bound P extracted by basic extractants.

There are at least seventeen different extraction methods used to assess P pools thought to be bioavailable in short- to medium-term (Harmsen, 2007), and several more targeting slowly available or immobile P pools. This diversity arises from the fact that methods have been developed in various soil types and for different applications, as it has been recognized very early on that no single extractant could give an accurate assessment of plant-accessible P in different mineral matrices (Rost, 1917). Thus, I argue that there is a need for a comparative evaluation and calibration for identifying the most appropriate P test for Newfoundland and Labrador soils with a distinct environmental conditions and ongoing agriculture expansion into forest areas to address provincial food security.

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1.4. Co-Authorship Statement

The project idea, and its relevance to the Newfoundland and Labrador and Atlantic Canada, was first proposed by Dr. Adrian Unc. The project work was conducted in the Agriculture and Agri-Food Canada (AAFC), St. John's Research and Development Centre research facility, and Provincial Soil and Feed Laboratory both located at 308 Brookfield Road, St. John's, Newfoundland and Labrador. Dr. David McKenzie was the contact person in charge of the soil and water research laboratory in the AAFC. Dr. McKenzie was also participated in a weekly advisory meeting on the experiment design held at the AAFC in 2018/2019 and facilitated the laboratory and fieldwork. I collected the soil samples from AAFC, St. John's research fields and Centre for Agriculture and Forestry Development (CAFD), Wooddale used in Chapter three to five, except for the Cormack soil samples used in Chapter three which were provided by Dr. Unc. During sample collection technical assistance to operate backhoe was provided by AAFC and CAFD. However, none of the field assistants were involved in the design of the project. The soil samples used in Chapter six was collected by Mr. Richard Tingskou for a common research project.

I handled and processed the soil test dataset used in Chapter two which obtained from Newfoundland farmers upon their permission. I independently developed and carried out each set of laboratory experiment and analysis of Chapter 3 to Chapter 5. The pot experiment in the greenhouse was jointly conducted with Mr. Tingskou.

At least once per academic year, full supervisory committee meetings were held to discuss each experimental design, corresponding results, and steps for moving forward with data interpretation and writing.

Once each experimental dataset was collected, interpreted, and discussed during regular weekly meeting with Dr. Unc, I prepared manuscript drafts (Chapter two to six) that were then shared with Dr. Unc for initial feedback before being circulated to Dr. Mumtaz Cheema, Dr. Kelly Anne Hawboldt, and Dr. Lakshman Galagedara. Feedback, concerns, and suggested revisions from all thesis committee are incorporated into the thesis Chapters.

Chapter 2. UNDERSTANDING SOIL FERTILITY IN NEWFOUNDLAND FROM STANDARD FARM SOIL TESTS

2.1. Abstract

Farm soil tests are common decision support tools employed by regulatory agencies and farmers to manage nutrients in an economic and environmentally sustainable way. The complex interplay between the local environment and locally relevant crops makes soil testing, and critically soil-test based recommendations, site-specific. The province of Newfoundland and Labrador (NL), with its relatively small but rapidly growing commercial agriculture has yet to develop locally calibrated test-based nutrient recommendations for its farmlands mainly converted over the last 80 years from boreal forest. A first step towards developing locally calibrated recommendations is understanding of current practices. For this I examined regular soil test reports and associated recommendations for Newfoundland (Nfld). Following a request distributed to 167 farmers 1503 soil tests were obtained from 32 farms. While tests exemplify the gamut of crops in Nfld more than half were from forage and mixed forage fields in western Nfld, representative of dairy farms. Results show that even in the absence of more comprehensive site analyses, an analytical survey of farm tests may be employed to identify possible environmental and economic inefficiencies of local cropping systems, including regional and crop type driven differences, for both nitrogen (N) and phosphorus (P) fertilization. Soil-test based identification of possible N and/or P inefficiencies, and associated crop and regional particularities, including excess fertilization, can be employed to devise targeted

research for improved, preventative decision tools for both environmental and economic sustainability.

Key words: soil management, soil fertility, Newfoundland, nitrogen, phosphorus

2.2. Introduction

The recommendation value of soil testing is rooted in the repeatedly verified relationships between the test results and the uptake of nutrients by plants (Fageria & Baligar, 2005; Jordan-Meille et al., 2012). The dynamics of these relationships vary widely as a function of a range of chemical and physical environmental parameters that govern the soil functions, as expressed through soil microbial activities, and which are dependent on the natural and management history of the site, and the local climatic parameters (Fageria & Baligar, 2005; Jones, 2001). Furthermore, the plant species and their varieties are selected and bred to match the local environmental conditions (Warncke et al., 2009). Consequently, the complex interplay between the local environment and locally relevant crops makes soil testing, and critically soil-test based recommendation, site-specific (Mallarino, 2005). This specificity is what drives the need for research that verifies local relationships between soil test, nutrient and occasionally more general management recommendations, and the productivity of the targeted agricultural crops. The yield response is used in an iterative, feedback-loop approach to calibrate the interpretation of the soil tests for improving management decisions (Benjannet, Nyiraneza, et al., 2018). When agriculture expands into new regions with novel climatic and edaphic conditions, and with either novel or imported crop varieties not always well adapted to the new environment, the relationship between

soil test results and recommendations is uncertain (Mehra et al., 2018). Critically, in Newfoundland, the evidence of the effect of recommendations, i.e., detailed yield data, is yet scarce thus hampering the iterative calibration of the test and recommendations. It must be here noted that while such soil tests are interpreted in a soil fertility context, or occasionally soil health context, these concepts are not explicitly integrated or directly addressed by farm soil tests (Kwabiah et al., 2005; Spaner et al., 2000; Spaner et al., 2001). Soil-testing targets physical, chemical, and biological soil characteristics. However, the selection of appropriate soil tests is challenging due to the complexity and heterogeneity of the soil and land uses (Bünemann et al., 2018). The most widely used soil fertility indicators are soil organic matter (SOM), pH, available phosphorus, water holding capacity and bulk density (Bünemann et al., 2018), with mineralizable nitrogen (ammonium and nitrate) species commonly evaluated close to planting.

Soil pH is key for contextualising nutrients' chemical speciation and their availability for specific crops. The pH regulates soil chemical reactions (adsorption-desorption, and dissociation-precipitation) and microbial activities (mineralization-immobilization of organic matter). The most favourable pH for nutrient availability ranges from 5.5-7.0 (Osman, 2013). In acidic soil, at a pH<5.5, the solubility of aluminium (Al), iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) increases, leading to Al toxicity, while calcium (Ca), magnesium (Mg), and molybdenum (Mo) decreases causing deficiencies (Jones 2002; Havlin et al., 2016). Furthermore, soluble Al, Fe, and Mn in acidic soil precipitate/adsorb dissolved P (Baker & Eimers, 2015) limiting plant-available phosphates. Commonly, soil pH measures active soil acidity which is the concentration of H^+ in the soil solution. Total soil acidity includes active acidity, exchangeable acidity, and residual

acidity. Of them, exchangeable accounts for the large proportion of acidity from cations H^+, Al^{3+}, Fe^{2+} and Fe^{3+} and it is the one used for calculating the lime requirement to raise the soil pH to the range favorable for cultivation (McLean 1982; Havlin et al., 2016). Hydrolysable organic matter that can contribute H^+ to the soil solution can also contribute to the total soil acidity.

Soil organic matter contributes to soil fertility by releasing plant required nutrient through mineralization. It also increases soil CEC, buffers soil. Furthermore, SOM bonds soil particles together to improve soil structure, aeration, water and nutrient retention capacity (Wang and Huang 2001).

The availability to plants of N, P, and potassium (K) determine the capacity of a soil to provide nutrition for farm crops. Nitrogen, P and K, the so called large three, are the most common cost nutrient inputs into crop production. Cumulative fertilization over long-term farming might lead to an accumulation of P in soil, which has a potential to be carried away by erosion or surface water runoff into rivers and lakes, causing eutrophication (Beauchemin & Simard, 1999; Pellerin et al., 2006). Available nitrogen in nitrate form is easily moved through leaching or runoff or denitrification in anaerobic conditions and therefore soil test for N is usually done close to planting for best estimating soil N capacity and hence to make reasonable N fertilizer recommendations.

In most cases, the status of soil fertility is evaluated through soil protocols tailored to soil types under the conjecture that matching test to soil best describes plant-available nutrients for the respective soil. Most soil tests measure the primary nutrients N, P, and K, pH, cation exchange capacity (CEC), SOM, Ca, Mg, Mn, sulfur (S), boron (B), Cu, Al, Fe, Mn, sodium (Na), and Zn (McGrath et al., 2014). The recommendations target the optimum economic

yield of the crops based on the region-appropriate expected yields and thus expected annual nutrient removal. Nutrient ranges and their economic maxima can vary by plant species, targeted plant part and growth stage (McGrath et al., 2014).

Furthermore, soil tests, while most widely used for agronomic ends, can also inform environmental risk assessments. For example, agronomic methods e.g. Olsen, Mehlich-3, Bray-1, weak organic acids, or diluted mineral acids used to measure available P in soils (Wolf and Baker 1985; Wuenscher et al., 2015) can be also employed for environmental quality purposes. The P saturation index (PSI), also known as the degree of P saturation or P saturation ratio, and soil P sorption capacity (SPSC), are developed for the P management to avoid excessive use of P (Jalali and Jalali 2017; Kleinman et al. 2017; Nyiraneza et al. 2017; Benjannet, Khiari, et al., 2018; Benjannet, Nyiraneza, et al., 2018).

Notwithstanding the wide global availability of well-established soil fertility tests, the soil test methods and their fertilizer recommendation are very soil type and crop specific. In the boreal regions of Newfoundland and Labrador (NL), where agriculture land is newly converted from forested Podzols (Canadian Soil Classification, 1999) to agricultural use, commercial agriculture is carried out on soils and in climates less desirable for agriculture. In NL commercial agriculture is relatively new, having truly expanded only after the 1950s (Spaner et al. 2000, 2001; Spaner and Todd 2004; Kwabiah et al. 2005). Most recently, the government of NL implements policies to increase local food production by at least 20 percent by 2022 through the incentivized expansion of agricultural land onto natural boreal forested lands (Government of Newfoundland and Labrador, 2017). Also, while NL employs soil and plant tests to assist agricultural production, through recommending fertilizer and lime requirements, the overall soil fertility status across the province has yet

to be fully evaluated. This gap in knowledge hampers understanding of the impact of agricultural practices on current lands and on newly converted lands on agricultural suitability, environmental sustainability, and thus future policies. For example, the recommended test for available soil P was Bray-2; in 2013 the province adopted the Mehlich-3 extraction method coupled with ICP-OES quantification as it allows for both P and micronutrients to be simultaneously measured (S. Elsworth, personal communication, 2020). If farmers provide manure samples, manure delivered nutrients are considered when fertiliser applications are recommended.

In this context it was hypothesized that a survey of farm soil tests may be employed to identify crop and regional particularities in the soil fertility status and especially in the putative status of N and P within the context of fertilizer recommendations. Thus, I (1) assessed a baseline of the soil parameters in the insular Newfoundland (Nfld) portion of the province as inferred from the information available in standard soil tests, (2) evaluated the relation between soil tests and fertility recommendations, (3) to provide an informed set of suggestions for the development of testable hypotheses relevant to the validation of the soil testing information, and thus to the development of recommendations.

2.3. Materials and Methods

Farmers' soil test reports were requested via the Agri-food Development branch of the Forestry and Agrifoods Agency of the province of Newfoundland and Labrador. The department mailed out a consent and request letter to 167 farmers. Eventually, 32 farmers allowed access to their soil test reports for research purposes. A total of 1503 site-year data sets (between year 2013 and 2016) were identified and summarised into spreadsheets for further analysis. The soil reports include farm name and address (excluded here for confidentiality reasons), farm size (hectare), crop types, soil analysis year, pH, CEC, percent organic matter, macro and micronutrients (mg L^{-1}), lime recommendation (t ha^{-1}) based on Adams-Evans soil buffer determination (Carter & Gregorich, 2008), and recommended nutrient application rates for phosphorus (as P_2O_5), N, and potash (K_2O) (kg ha^{-1}) (Figure 2. 1).

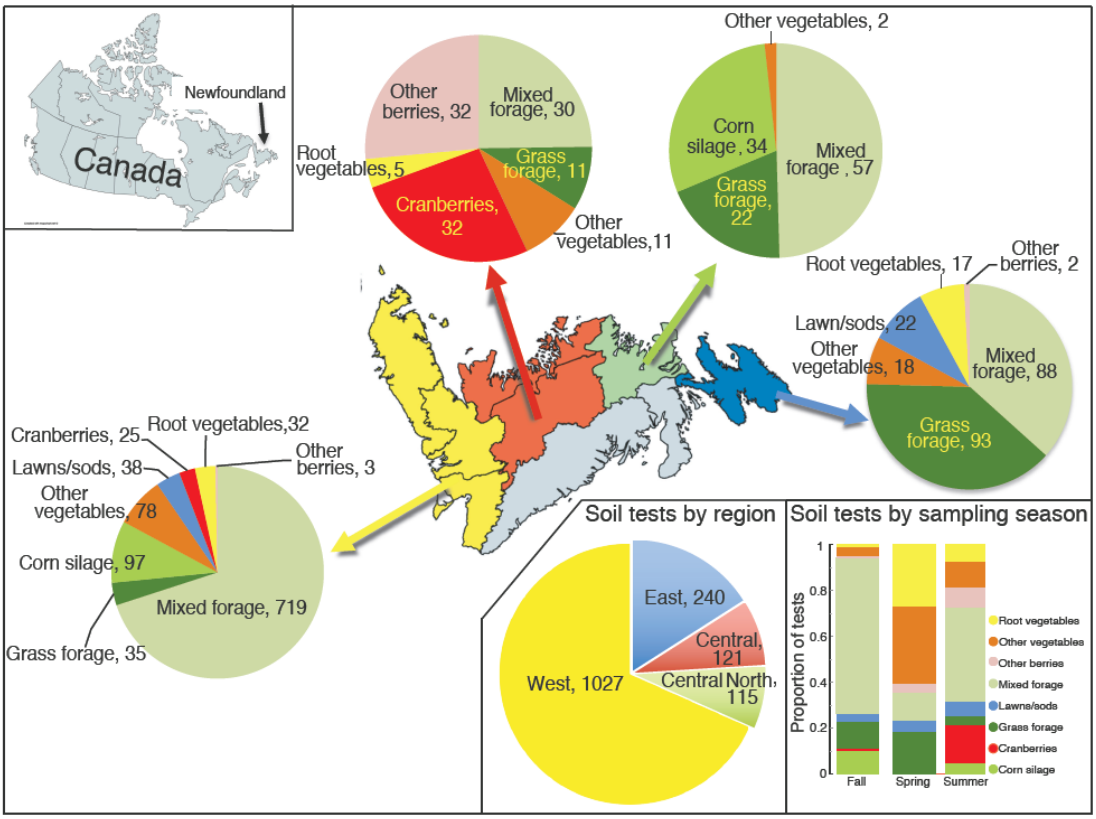

Figure 2. 1. Soil tests distribution by regions, crops, and sampling season (n=1503).

2.3.1. Soil Testing in Newfoundland and Labrador

Farm soils samples are usually collected by either farmers or by agents of a commercial fertilizer firm in the spring, summer or fall after which samples are sent to the provincial soil and plant analysis laboratory for routine analysis. The samples may arrive at the laboratory up to a week after sampling. The soil sampling details like soil depth, representativeness of the soil samples for each field, and sample handling before shipping are not known and it may vary from farm to farm. However, it is expected that soils are collected from the top 0-15 cm, and the samples are shipped to the laboratory for drying within few days after sampling.

Upon reception, soils are dried at 40 °C in an oven for 48 hr, passed through a 2 mm sieve and then stored at room temperature (23 °C) until analysed (T. Fagner, personal communication, 2019). The provincial soil and plant analysis laboratory employs the following methods: pH determined in 1:1 soil/water ratio (Soil Survey Staff, 2014); soil organic matter (SOM) based on loss-on-ignition method at 430 °C for 6 hr (Carter & Gregorich, 2008; Jones, 2001; Kalra & Maynard, 1991); milliequivalents of calcium, magnesium, and potassium measured in Mehlich-3 solution and the Adam-Evans soil pH buffer determination (Huluka, 2005; Ross & Kettering, 2011) are used to calculate the cation exchange capacity (CEC); lime recommendation determined from Adam-Evans pH soil buffer determination (Adams & Evans, 1962; Huluka, 2005); micro and macronutrients are extracted by the Mehlich-3 solution (Mehlich, 1984) and quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Carter & Gregorich, 2008; Jones, 1977).

2.3.2. Data Processing

Data was anonymized by removing farm ownership and address information.

The phosphorus saturation index (PSI) (Eq. 2.1 and 2.2), soil phosphorus saturation capacity (SPSC) (Eq. 2.3), cation exchange capacity (Eq. 2.4), aluminium saturation (AS) (Eq. 2.5) and the base saturation (BS) (Eq. 2.6) were calculated. A critical PSI-1 of 0.14 was identified, corresponding to the environmental limit of 200 mg P kg^{-1} (Mehlich-3 P) as recommended by the United States Department of Agriculture (Howard, 2006).

$$Phosphorus\ Saturation\ Index\ (PSI-1) = \frac{M3{-}P\ (\frac{mmol}{kg})}{M3{-}Al\ (\frac{mmol}{kg})} \qquad \text{Eq. 2.1 (Khiari et al., 2000; Szara et al., 2018)}$$

$$Phosphorus\ Saturation\ Index\ (PSI-2) = \frac{M3{-}P\ (\frac{mmol}{kg})}{M3{-}(Al+Fe)(\frac{mmol}{kg})}$$ Eq. 2.2

(Benjannet, Khiari, et al., 2018; Benjannet, Nyiraneza, et al., 2018; Khiari et al., 2000; Szara et al., 2018)

$$Soil\ Phosphorus\ Storage\ Capacity\ (SPSC) = (critical\ PSI - soil\ PSI) * (Al+Fe)moles$$ Eq. 2.3 (Nair & Harris, 2014)

$$Cation\ Exchange\ Capacity\ (CEC), = \left(\frac{ppm\ Ca}{200} + \frac{ppm\ Mg}{120} + \frac{ppm\ K}{390}\right) + 8 * (8 - buffer\ pH)$$ Eq. 2.4 (Huluka, 2005; Ross & Kettering, 2011)

$$Aluminium\ Saturation\ (AS)(\%) = \left(\frac{Aluminium\ cation}{CEC}\right) * 100$$ Eq. 2.5

$$Base\ Saturation\ (BS)(\%) = \left(\frac{Base\ Cations}{CEC}\right) * 100$$ Eq. 2.6 *(Omueti, 2016)*

Furthermore, given that the soil mineralizable N was not measured, the SOM values were used to estimate the mineralizable N in the soils, assuming a C to N ratio of 10 to 1 and also that 58% of the SOM is organic carbon (Pribyl, 2010). Furthermore the following assumptions were made: a) organic matter (OM) bulk density of 0.22 g cm^{-3} and mineral soil bulk density of 1.4 g cm^{-3} (Rawls, 1983); b) about 5.8% of SOM is organic N (i.e., C:N ratio of 10) of which 1.5% of organic N is annually mineralisable (United States Department of Agriculture (USDA), 2012); c) there is an about 20% mineralisation suppression from nitrogen fertilizer (Mahal et al., 2019); and d) a soil depth of 0 - 0.15 m is considered; unit conversion factors were applied (percent to mg kg^{-1}, g cm^{-3} to kg m^{-3}, and mg m^{-2} to kg ha^{-1}).

$$Estimated\ N, \frac{kg}{ha} = SOM(\%) * BD(g\ cm^{-3}) * Depth\ (m) * 0.058 * 0.015 * 0.8 * 10000(mg\ kg^{-1}) * 1000(kg\ m^{-3}) * 0.01(kg\ ha^{-1})$$ Eq. 2.7

Soil bulk density, $BD(g\ cm^{-3}) = \frac{100}{\frac{SOM(\%)}{OMBD(g\ cm^{-3})} + (100 - \frac{SOM(\%)}{MBD(g\ cm^{-3})})}$ Eq. 2.8

where SOM is soil organic matter in percentage, OMBD is organic matter bulk density (g cm^{-3}) and MBD is mineral bulk density (g cm^{-3}).

2.3.3. Statistical Analyses

The data were analyzed using descriptive, exploratory, and predictive analyses using PAST3 (Hammer, 2006) and SPSS vs. 25 (SPSS Inc, 2017). Mean comparisons between relevant groupings were carried out using a generalized linear model by applying a Tukey HSD post-hoc test. Pearson correlations were calculated between soil variables and recommendations. Multiple linear regressions were employed to predict the lime and nutrients (NPK) recommendation using soils test variables as independent variables based on the strength of correlation and correlation matrices loading.

2.4. Results and Discussion

The 1503 soil test data sets from 32 farms across the province were obtained from the farmers' soil test reports between 2013 and 2016. Newfoundland and Labrador had a total of 407 farms in 2016, down from 643 in 2001 but with an actual increase in total agricultural land (Statistics Canada, 2020). The dataset represented 8% of the 2016 farm numbers but covered nearly the entire gamut of the farming types at proportions similar to their representation among all farms; poultry farms were not represented.

No information was available on the fertilizer types and farm age. Despite these uncertainties, data was classified by crop groups and geographic regions: 29 crops were summed into eight major groups: *mixed forages* (59.5%), *grass forage* (10.7%), *corn silage* (8.7%), *other vegetables* (7.3%; included beans, peas, sweet corn, pumpkin, peppers, cole crops, cucumbers, lettuce, mixed vegetables, onions, spinach, squash, and tomatoes), *lawns/sods* (4.0%), *cranberries* (3.8%), *root vegetables* (3.6%; included beets, carrots, potatoes, and turnips), and *other berries* (2.4%; included strawberry and blueberry) (Figure 2. 1). Most farms that grow forage crops are dairy farms; 11 farms grow two or more crops (Figure S2.1). It was reported that the forage production in NL satisfies about 85% of the dairy industry demand for animal feed (Cordeiro et al., 2019). Mixed forage was dominant in each of the four agricultural regions. Thus, in addition to all crop categories, the *mixed forage* datasets were used to evaluate the regional soil test variation (Table 2.2). About 75% of the soil tests are sampled in the fall season sampling uniformly across years, regions, and crop groups (Figure 2. 1). Most datasets (68.3%) represent western Newfoundland fields, with *mixed forage* dominant (Figure 2. 1).

2.4.1. Soil pH

The soil pH ranged from 3.8-8.1 where about 80% of the tests had a pH>5.5 comparable with the pH range of 4.6-6.6 for most cultivated mineral soils of the Maritime provinces (NL Forestry and Agrifood Agency, 2018). Soil pH varies with crop types and thus management. For example, the *corn silage* plots had significantly higher soil pH (6.4±0.1) than *lawns/sods* (6.1±0.3), *mixed forage* (5.9±0.0), or *grass forage* (5.9±0.1) (Table 2. 1). Among all crops soil pH was directly correlated with soil Mg, Ca, base saturation (BS), K, S and P, but inversely correlated with Fe, Al, N:P ratio, Al saturation (Al sat) (Table S2.3 and Figure 2.2). As it was expected, the soil pH informs, and thus is significantly ($p < 0.05$) correlated with, lime recommendations but also with the phosphate (P_2O_5) and potash (K_2O) recommendations (Table S2.5) (Nanda & Nascente, 2014).

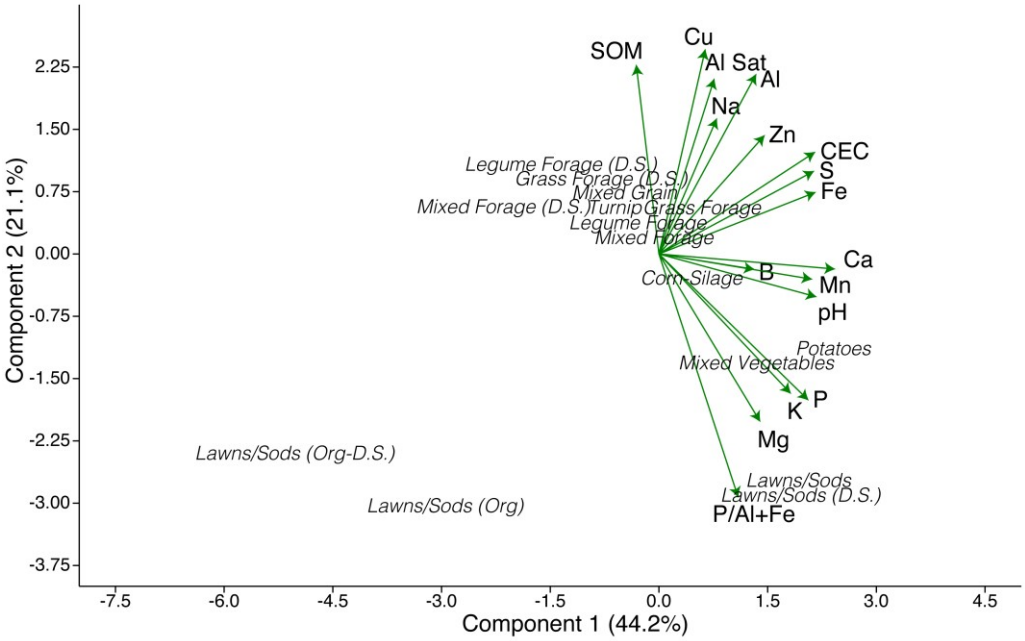

Figure 2.2. Soil parameters for the most common crops; principal component analysis (PCA) biplot of soil test variables based on a correlation distance matrix.

2.4.2. Cation Exchange Capacity

The mean CEC of crop groups follow order of *cranberries* << *lawns/sods* ≤ *corn silage* ≤ *root vegetables*, *other vegetables*, and *mixed forage* ≤ *grass forage*. Cranberries are cultivated on bog peats topped with a bed of sand which has a lower cation concentrations (Vander Kloet, 1988). The *grass forage*, and *mixed forages* fields might receive regular liming and manure applications. I can conjecture that the type of crop and related management greatly influences the soil's CEC across the regions. For example, the lower average CEC in the soils of the central region reflects the dominance of cranberry fields in the collected soil tests. Moreover, the factors' two-way interaction confirmed that the overall significant differences of CEC were associated with crop groups (Table S2.6). Nevertheless, even for the same crop, i.e., *mixed forage*, the CEC varies regionally (Table 2.2).

2.4.3. Iron, Aluminium, and Calcium Distribution

The soil Fe content in *mixed forage* soil was not significantly ($p > 0.05$) different from the *other vegetables*, *root vegetables*, *grass forage*, and *cranberry*, but was significantly ($p < 0.05$) greater than for *other berries*, *corn silage*, and *lawns/sods* (Table 2. 1). Also, a similar trend was observed for Al except for the Al from *cranberry* plots, which was significantly ($p < 0.05$) lower than for all other crop groups (Table 2. 1). As with the K trend, the Ca in the cranberry soil test was significantly ($p < 0.05$) lower than for other crops (Table 2. 1). The Ca in *cranberry* field soils implies the leaching of cations from the surface soil. Generally, soils of *other berries* and *vegetables* have significantly higher Ca than other crops (Table 2. 1).

Furthermore, the soil from western Nfld *mixed forage* fields have significantly ($p < 0.05$) higher Fe and Ca content than in other regions (Table 2.2). On the other hand, the *mixed forage* fields of the central Nfld have available Al contents significantly higher than for other regions (Table 2.2), which might be related to the lower lime usage in the region (Table S2.1).

Aluminium concentrations were negatively correlated with most soil variables but positively correlated with lime and phosphate recommendations and calculated Al sat index. Contrary to Al, soil Ca was positively correlated with all soil test variables except Fe while negatively correlated with Al, Al sat, lime, phosphate, and potash recommendations (Table S2.3, Table S2.4 and Table S2.5)

Table 2. 1. Soil test variables by crop groups (Mean ± 95% confidence interval).

Crop groups	pH	SOM	CEC	P	K	Fe	Al	Ca	PSI 2 (P/Al)	PSI 2 [P/(Al+ Fe)]
		%	cmol kg^{-1}	mg kg^{-1}					mM ratio	
CORN SILAGE (n=131)	6.4± 0.1^{a}	5.5± 0.3^{a}	14.6± 0.6a	134± 15^{a}	191± 18^{a}	199± 6^{a}	1279± 32^{a}	1566± 85^{a}	0.09± 0.01^{a}	0.09± 0.01^{a}
CRANBERRY (n=57)	6.2± 0.2 ^{b,a}	na	7.0± 1.1^{b}	84± 19^{a,b}	52± 9^{b}	235± 31^{a,b}	727± 136^{b}	943± 221^{b}	0.26± 0.10^{b}	0.15± 0.05^{b}
GRASS FORAGE (n=161; for OM n=156)	5.9± 0.3^{c}	6.9± 0.3^{b}	16.8± 0.6^{c}	129± 28^{a,b}	145± 17^{c}	244± 14^{b,c}	1360± 46^{a}	1564± 151^{a}	0.10± 0.03^{a}	0.09± 0.02^{a}
LAWNS/SODS (n=60; for OM n=38)	6.1± 0.3 ^{b,c}	3.4± 0.2^{c}	13.5± 1.2^{a}	242± 48^{c}	246± 41^{d}	209± 23^{a,c}	892± 149^{c}	1300± 160^{a}	0.28± 0.08^{b}	0.20± 0.04^{c}
MIXED FORAGE (n= 881 to 894)	5.9± 0.0 ^{c}	6.1± 0.1^{d}	16.1± 0.2^{c}	75± 4^{a}	118± 5^{e}	255± 6^{b}	1308± 18^{a}	1301± 35^{a}	0.06± 0.00^{c}	0.05± 0.00^{d}
OTHER BERRIES (n=37)	6.2± 0.2 ^{a,b}	6.3± 1.0^{a,b,d}	16.3± 1.6^{a,c}	191± 42^{a,b,c}	136± 20^{c,e}	189± 9^{a}	1313± 93^{a}	2171± 326^{c}	0.14± 0.04^{a,d}	0.13± 0.04^{a,b}
ROOT VEGETABLES (n=52 to 54; for OM n=38)	6.1± 0.2^{a,b,c}	7.3± 1.5^{b}	15.4± 1.3^{a,c}	227± 92^{c}	132± 41^{c,e}	248± 30^{b,c}	1309± 121^{a}	1744± 61^{a,d}	0.18± 0.07^{d}	0.15± 0.06^{b}
OTHER VEGETABLES (n=97 to 109; for OM n=74)	6.2± 0.2 ^{a,b}	5.6± 0.7^{a,d}	15.7± 1.0^{a,c}	198± 51^{c}	158± 35^{a,c}	252± 20^{b}	1181± 80^{a}	1921± 199^{c,d}	0.18± 0.05^{d}	0.15± 0.04^{b}

The same letter in the same column indicates statistical similarities for means at alpha of 0.05. Nutrients (P, K, Fe, Al, and Ca) extracted with Mehlich-3 and anaysed with ICP-OES.

Table 2.2. Soil test variables by region for the mixed forages (Mean ± 95% confidence interval). The same letter in the same column indicates statistical similarities for means at alpha of 0.05.

Nfld Regions	pH	SOM	CEC	P	K	Fe	Al	Ca	*PSI 1* (P/Al)	*PSI 2* [P/A(l+Fe)]
		%	cmol/kg	mg kg^{-1}					mM ratio	
East (n=88)	5.8± 0.1[a]	8.2± 0.8[a]	13.7± 0.8[a]	79.6± 21.4[a]	111± 20[a]	230± 17[a]	1326± 53[a]	1128± 130[a]	0.06± 0.02[a]	0.05± 0.02[a]
Central (n=30)	5.8± 0.3[b]	4.7± 1.0[b]	14.5± 1.2[a]	45.1± 22.7b	48± 10[c]	118± 24[b]	1705± 59[b]	1100± 295[a]	0.06± 0.01[a]	0.06± 0.01[a]
Central North (n=57)	5.8± 0.2 [a]	6.9± 0.5[c]	14.9± 0.8[b]	88.7± 19.6[a]	162± 33[d]	207± 25[a]	1373± 51[a]	1195± 174[a]	0.06± 0.02[a]	0.05± 0.02[a]
West (n=719)	6.0± 0.0[b]	5.9± 0.1[b]	16.7± 0.2[c]	76.4± 3.9[a]	123± 4[a]	263± 7[c]	1286± 20[a]	1331± 35[b]	0.06± 0.01[a]	0.06± 0.01[a]

2.4.4. Soil organic matter

The overall SOM ranges from 1.7% to 27.8%, with a mean of 6.1% (±0.12, 95% confidence interval) for the 1503 datasets (data not presented). The average SOM in the soils managed under forage crops (*grass forage*, *mixed forage*, and *corn-silage*) was comparable with the SOM in the perennial rotation pasture soils of northern-central Nova Scotia (Bouman et al., 2018). More than 65% of the samples reported in this study had a SOM < 5%, and can be thus classified as mineral soils (Von Lützow et al., 2002). The mean of SOM was significantly ($p < 0.05$) different among crop groups and regions (Table 2. 1 and Table 2.2), which is often used as an indicator of the regional variability in soil and most importantly of the impact of crop-specific management on soils (Sena et al. 2002; Havlin et al., 2016). The SOM in the plots of *root vegetables* (7.3±1.5%), *grass forage* (6.9±0.3%), and *other berries* (6.3±1.0%) was significantly ($p < 0.05$) higher than for *lawns/sods* (3.4±0.2%) (Table 2. 1). The lower SOM in *lawns/sods* could be related to the application of mineral fertilizers and minimal return of plant residue to the soil while the plots of *root vegetables* and *grass forage* might receive large amounts of manures. Eastern Nfld tests results have

shown significantly ($p < 0.05$) higher SOM than for the other regions. The mean SOM decreased along the series east>>central north>central≥west Nfld ($p=0.05$) (Table 2.2). The interaction between crop groups and regions confirmed that the *mixed forage*, *other berries*, and *root vegetable* fields in the eastern region contributed to the higher average SOM compared to other regions (Table S2.6). Additionally, the regional climate and soil variations might contribute to the SOM differences (Von Lützow et al., 2002). The SOM of *mixed forage* plots ($n = 894$) was the largest driver for the differences between the regions, which might be an indication of the role of climate and soil driving SOM variation between the regions.

The SOM has a significant ($p < 0.05$) positive correlation with most cations, specifically sodium (Na) (Table S2.3). The latter might be employed as a proxy for manure application, as it does not naturally occur in boreal soils but it is common in animal feed (Rivas Lucero et al., 2018). Thus, higher SOM might signal more manure applied to fields, common for dairy farm forage fields. When all data was combined the SOM was weakly or not correlated with phosphorus and potassium concentrations. However, when only the *mixed forage* data was analysed the relationship became significant (Table S2.4).

2.4.5. Estimation of Mineralizable Organic Nitrogen in Soil Organic Matter

The SOM mineralization in boreal Podzols is expected to increase as temperature increases (Moni et al., 2015). The current N recommendation in Nfld do not account for plant mineralizable N released from SOM over the growing season. In this study, I estimated the mineralizable organic N. Therefore, the estimated mineralizable N from SOM ranges from

29 to 123 kg N ha^{-1} for soils managed under *corn silage*, 53 to 140 kg N ha^{-1} for *grass forage*, 40 to 68 kg N ha^{-1} for *lawns/sods*, 41 to 168 kg N ha^{-1} for *mixed forage*, , 65 to 120 kg N ha^{-1} for *legume forage,* 52 to 190 kg N ha^{-1} for *potatoes*, and 37 to 149 kg N ha^{-1} for *mixed vegetables* (Figure 2.3). The natural soil conditions and crop related management, but also variable access to manure, may explain such wide variations.

The local N fertilisation recommendations do account for availability of manure N, if the farmers provide a manure sample, but do not account for mineralizable SOM. The total recommended N rates are solely recommended on crop type. In this survey, the lowest recommended N fertiliser rate (20 kg N ha^{-1}) was noted for fields managed under *legume mixed forages* (which include pea) while the highest N was recommended for *grass forages* (165-180 kg N ha^{-1}) (Figure 2.3) and cole crops (220 kg N ha^{-1}, data not presented). Nevertheless, the putatively available SOM-N might be 2 to 3 times above the amounts of the recommended fertilisation rates (Figure 2.3). This implies the need to better understand mineralizable N in the soils, including priming effects and how these vary with the quality of the soil OM (Mahal et al., 2019). Furthermore, while SOM mineralisation rates were estimated, the use of manure, common on dairy farms and poultry farms in the province, might deliver organic matter that mineralises significantly faster and thus raising the amounts of soil available N significantly higher. Depending on the timing of the soil sample collection versus the timing of manure application the OM types and quality may vary. For example, compost may mineralise at an annual rate of about 18% while swine and poultry manure may mineralise at annual rates of 55% (Eghball et al., 2002). It has been previously estimated that the dairy farms in NL could supply 30 to 80% of their own N needs, depending on what manure management options are implemented (Butler et al., 2017).

While pre-seeding soil testing for available N might be considered it is well known that these tests are very sensitive to sample handling and also rarely representative of the availability in the field over the length of a cropping season (Dessureault-Rompré et al., 2015).

Nevertheless, soil mineralisation might be predictable from measured SOM (Dessureault-Rompré et al., 2010), and thus this is a reasonable recommendation for future work on Podzols of variable land-use conversion ages. Thus, the uniform crop based N recommendations (Figure 2.3) do not account for the soil mineralizable N and thus there is a disconnect between the soil fertility as indicated by SOM and N fertilisation. The SOM in the eastern Nfld mixed forage plots was almost twice the SOM of the plots for the same crop in central Nfld, but the N recommendation of 100 kg N ha^{-1} was uniform across the province (Figure 2.3). The SOM differences might be related to the fields' management history, its age from conversion and availability of manure. A uniform N rate recommendation for each crop is common for all crops (Figure 2.3).

Furthermore, the C:N ratios, a proximate indicator of mineralisation potential, varies widely with the soil conversion status and management. A newly converted Labrador soil has an estimated C:N ratio of about 52, based on the 3% SOM and 0.033% N as measured in 0-15 cm soil (Kirkby et al., 2011), while a C: N ratios of 14, 16, and 11 were measured for managed Ap, B, and C soils horizons at the Agriculture Agri-Food Canada, St. John's Research and Development Centre research plots (Chapter 4).

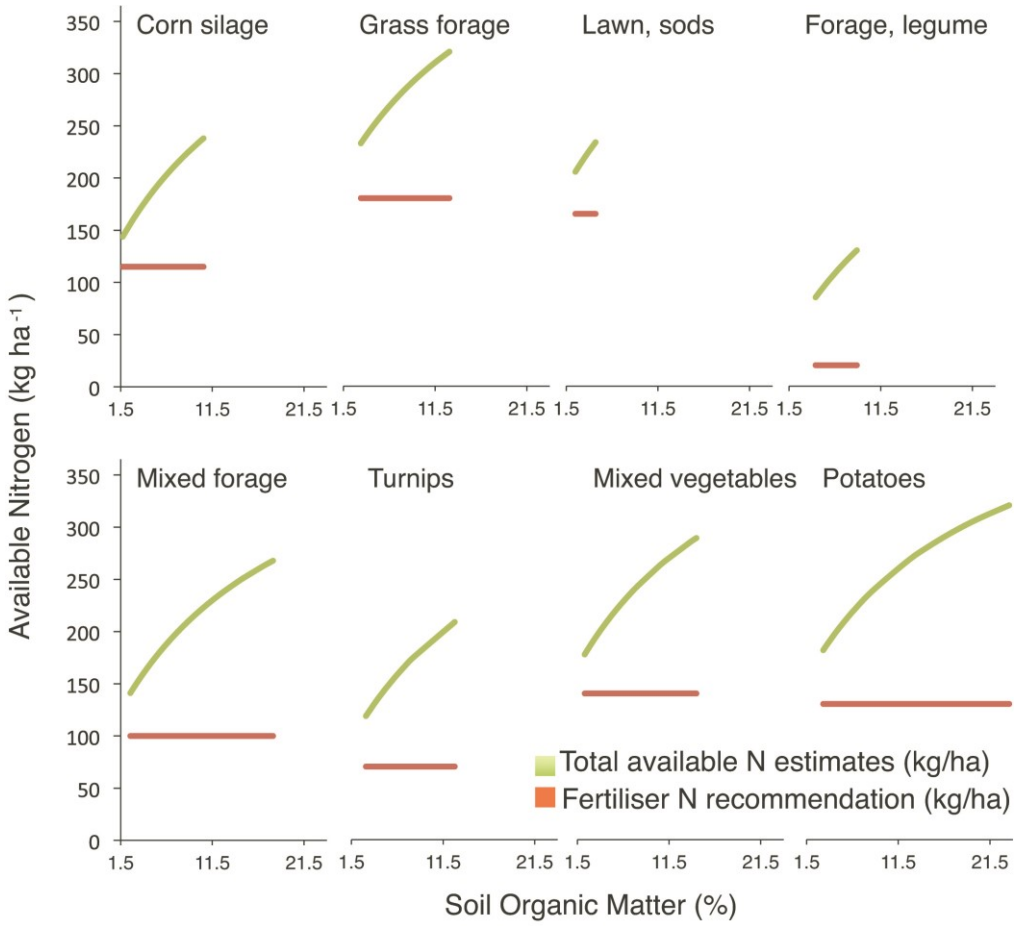

Figure 2.3. Recommended and estimated availability of organic N; the total estimates include recommended N fertiliser and estimated mineralizable (available) N in SOM.

2.4.6. Soil phosphorus

The available soil phosphorus (P), as measured by the Mehlich-3 method, is employed to recommend P fertilizer rates in the province. A general linear model (GLM) univariate analysis grouped the Mehlich-3 P into three crop subsets: (i) *mixed forage* and *cranberry*; (ii) the *grass forage* and *corn silage*; and (iii) *other berries*, *other vegetables*, *root vegetables*, and *lawns/sods* (Table 2. 1). The last set had a significantly ($p < 0.05$) higher mean Mehlich-3 P than the first two sets. Specifically, the mean Mehlich-3 P followed the sequence: *lawns/sods* > *root vegetables* > *other vegetables* > *other berries* > *corn silage* >

grass forage > *cranberry* > *mixed forage* (Table 2. 1). The need for uniformity and consistency of grasses grown in lawns/sods farms might lead to excessive mineral P fertilisation. Remarkably, no significant ($p > 0.05$) differences were observed between the mean Mehlich-3 P concentrations across the regions, an analysis that nevertheless depends on the regional variability in *mixed forage* represented in the available regional dataset. This suggests crop dependent P fertilizer recommendations (Nova Scotia Department of Agriculture 2010).

Based on the P ratings for the general crops adopted from Nova Scotia, 23% of the soil tests have ≤31 mg P kg^{-1} (upper limit of the lower P range), 59% have ≥58 mg P kg^{-1} (lower limit of the higher range), and 24% have ≥135 mg P kg^{-1} (upper limit of the excessive P range) (Figure 2.4). These P rating categories reflect the fact that most farms have a high or excessive soil P. About 45% and 50% of the soil tests have Mehlich-3 P exceeding the Québec's 66 mg Mehlich-3 P kg^{-1} (Carefoot & Whalen, 2003) and Alberta's 60 mg P kg^{-1} (Howard, 2006) agronomic critical limit, respectively.

About 12% of the soil P tests were greater than the upper recommended limit (i.e., 200 mg P kg^{-1}) for environmental protection (USDA 2012 and Benjannet, Khiari, et al., 2018). The reduction of P application is recommended for Prince Edward Island acidic soils with the P greater than 200 mg P kg^{-1} to prevent the P losses from the farms (Benjannet, Khiari, et al., 2018). This signals the need for better understanding of the P dynamics in the Nfld old and recently established agricultural soils and calibrate the P analysis protocol in the context of Nfld soils.

Furthermore, the soil P is significantly ($p < 0.05$) correlated with K, Ca, Zn, pH, S, CEC, and N recommendation while negatively correlated with Al concentrations, and lime,

phosphate (P_2O_5) and potash (K_2O) recommendations (Table S2.3, Table S2.4 and Table S2.5). The PCA matrices based on biplot confirmed a similar P relationship with other soil variables (Figure 2.2).

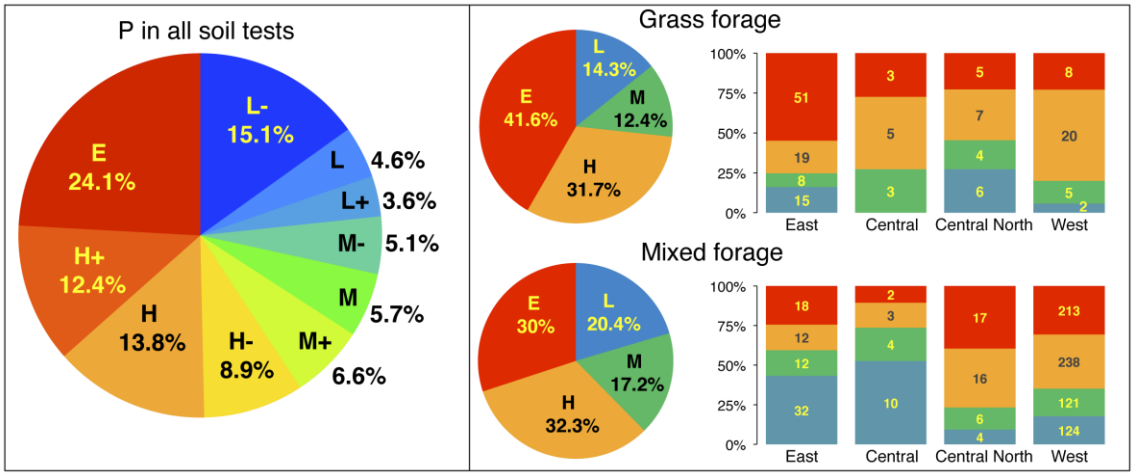

Figure 2.4. Proportional distribution of Mehlich-3 P (mg kg^{-1}) across all soil tests and the total and regionally distributed P for two crops common across all regions of Newfoundland, i.e., grass forage and mixed forage. P concentration ratings (mg kg^{-1}) for all tests: L-, <22.00; L, 22.01-27.00; L+, 27.01-31.00; M-, 31.01-36.00; M, 36.01-41.00;M+, 41.01-47.00;H-, 47.01-58.00;H, 58.01-72.00; H+, 72.01-90.00;E, >90.00. P concentration ratings for the forage samples: L, <31.01; M, 31.01-47.00; H, 47.01-90.00; E, >90.00. Test counts are listed for the regional descriptions. The ratings (L, low; M, medium; H, high) as employed by the Newfoundland and Labrador Department of Fisheries and Land Resources for general crops (adopted from Nova Scotia Department of Agriculture and Fisheries, September 2008).

2.4.7. Soil Phosphorus Saturation and Storage Capacity

The phosphorus saturation index (*PSI*) was calculated from the ratio of P to Al (*PSI-1*) or P to the sum of Al and Fe (millimolar) (*PSI-2*) representing crop groups, as presented in Table 2. 1. The *PSI-1* for *cranberry* and *lawns/sods* were significantly ($p < 0.05$) higher than for all other crop groups listed in Table 2. 1. Also, *lawns/sods* soils have significantly ($p < 0.05$) higher *PSI-2* than all other crop groups, which indicates lower content of Fe in the *lawns/sods* plots.

Generally, plots managed for forages (*corn silage*, *grass forage*, and *mixed forage*) have significantly ($p < 0.05$) lower *PSI-2* compared to other crop groups (Table 2. 1). The plots in the eastern and central regions have significantly ($p < 0.05$) higher *PSI-1* and *PSI-2* than for the central north and west regions (data not presented). This could be assigned to management differences i.e., crop and farm types. Surprisingly, the *mixed forage* plots have consistent *PSI*'s across Nfld (Table 2.2).

A stronger relationship was noted between *PSI's* and Mehlich-3 P when soil tests were with SOM<5%, were stratified by soil pH with pH<5.5, or >5% (Figure 2.5a&b). Based on the correlation between Mehlich-3 P and *PSI-1* for pH<5.5 and pH>5.5, the *PSI-1* corresponding to the recommended environmental limit (i.e., 200 mg P kg^{-1} for Mehlich-3 extractable P) was 0.20 and 0.24, respectively (Figure 2.5a). These indices were greater than the environmental *PSI-1* determined in PEI soils which were reported at 0.19 and 0.14 for soils with pH<5.5 and pH>5.5, respectively (Benjannet, Khiari, et al., 2018). Furthermore, the environmental P indices by regions showed greater variations (Table 2.2). The *PSI-1* for the soil tests from central north and western Nfld corresponds to 0.14 and 0.20, while the central and eastern regions have 0.33 and 0.36, respectively (Figure 2.5d). This was likely related to the variable proportions of crop types, and thus related management, in the dataset. Nevertheless, specific limits must be considered for both agronomic and environmental purposes. The soil tests from the central region have a similar environmental *PSI-1* (0.14) with the recommended agronomic P indices for potato management (Benjannet, Nyiraneza, et al., 2018) and for environmental indices in PEI soils (Benjannet, Khiari, et al., 2018). This value is also similar to the environmental index (0.15) recommended for Quebec soils (Khiari et al., 2000).

Additionally, a *PSI 1* of 0.14 or 0.18 was identified for the soil tests with SOM <5% or SOM>5%, respectively (Figure 2.5b). This suggests a *PSI-1* of 0.14 for environmental protection while 0.10 can be adopted for agronomic purposes (similar to PEI). About 17% of the soil test has P index greater than 0.14, which might suggest a risk of P losses. However, further evaluations require a better understanding of the soil P retention capacity and extractability specific to Nfld soils coupled with a better understanding of P dynamics in natural and managed podzol soils. The relationship between P index and soil Mehlich-3 P was related to soil pH, SOM and crop groups (R^2 ranged from 0.002 to 0.98) (Figure 2.5a-d).

Further, the remaining P storage capacity of the soils (SPSC) was calculated based on Eq. 2.3. As shown in Figure 2.6, positive SPSC reflects residual capacity of soil to store or adsorb P, and can help identify soils with apparently lower P sorption capacity, whereas the negative SPSC indicates that the soils storage capacity was exceeded, based on the recommended soil P limit for environmental protection (200 mg P kg^{-1} extracted with Mehlich-3) (Nair & Harris, 2014). About 14% of the soil tests have a negative SPSC. The combination of excessive Mehlich-3 P and low or negative P storage capacity indicates that P management must be adapted to prevent the risk of P loss to the environment.

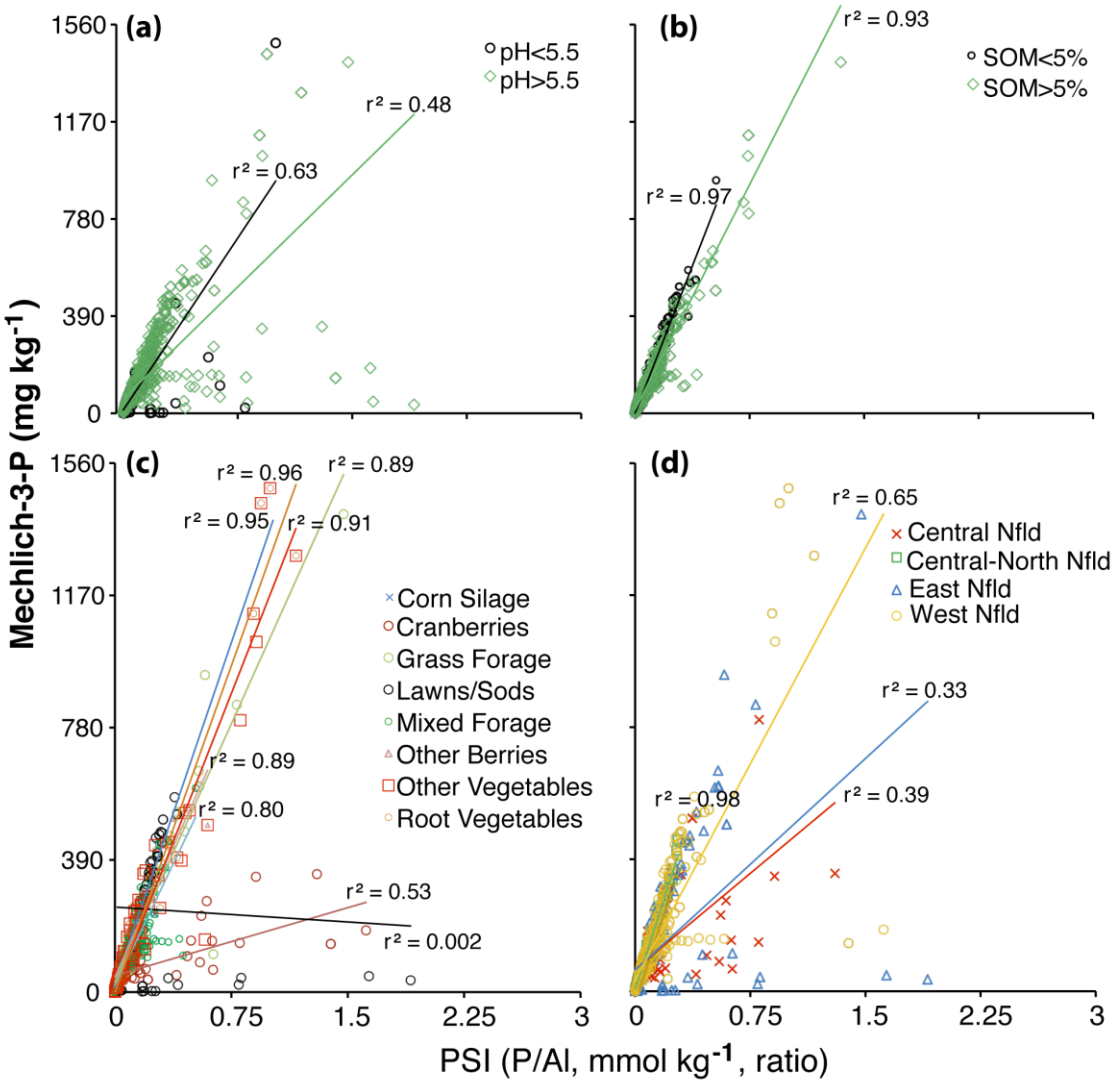

Figure 2.5. Correlation between Mehlich-3 extractable P and phosphorus saturation index (PSI=P/Al, mmol kg^{-1} ratio) for (a) soil pH greater or less than 5.5, (b) SOM greater or less than 5%, (c) crop groups and (d) regions.

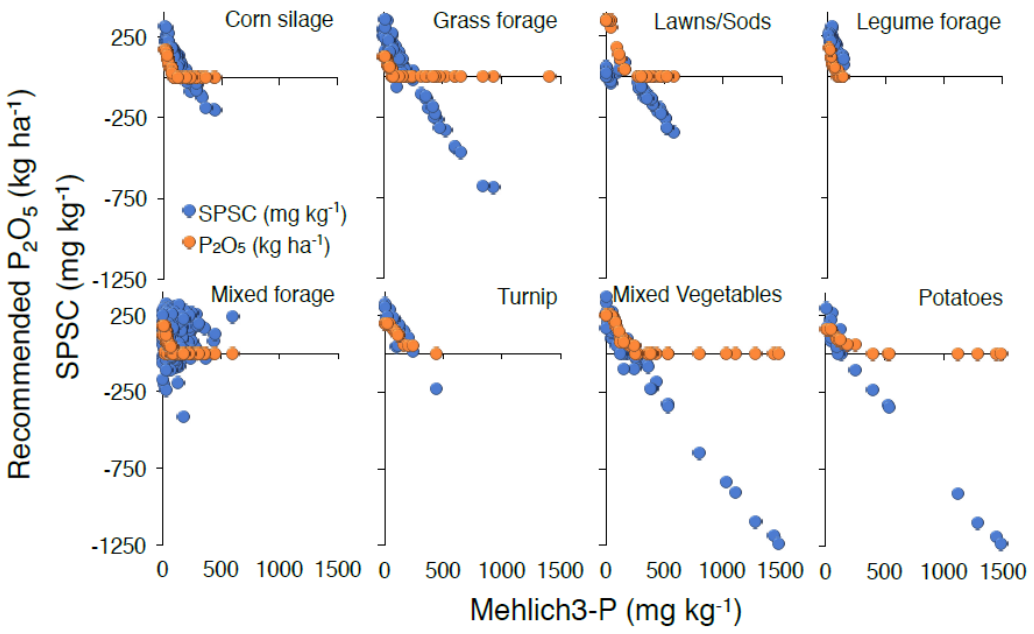

Figure 2.6. Relationship between Mehlich-3 P and soil P storage capacity (SPSC) and P_2O_5 recommendations for major crops.

2.4.8. Potassium Distribution

The *lawns/sods* soils have significantly ($p < 0.05$) higher mean K than the other crop groups (Table 2. 1), which might be linked to receiving of large amounts of NPK fertilizers to grow quality grass in short periods. Also, the *corn silage* has a significantly ($p < 0.05$) higher mean K in the soil than other crop groups but lower than *lawn/sods* (Table 2. 1). The mean K in the soils of *mixed forage*, *root vegetables*, *other berries*, *grass forage*, and *other vegetables* were not significantly different (Table 2. 1). The soils managed under *cranberry* have significantly ($p < 0.05$) lower mean K than other crop groups (Table 2. 1). This might be related to the flooding of the *cranberry* fields during harvest, where the K might be leached out from the topsoil. As most of the *cranberry* fields are in the central Nfld, the mean K for the central Nfld was significantly ($p < 0.05$) lower than in other regions (data not presented).

On the other hand, the K in the north-central Nfld soils was twice the K in the central Nfld soils (data not presented). This could be explained by lower K uptake by *corn silage*, *grass forage*, and *mixed forage* which represented the region. This assumption was confirmed by comparing the mean K for *mixed forage* alone between the regions (Table 2.2). This might be related to the regional variation of mineral K in the soils. Moreover, K in the soils of all crops and *mixed forage* had a positive correlation with most soil test variables, whereas it was negatively correlated with iron, Al sat, lime and nutrient recommendation except N recommendation (Table S2.3, Table S2.4 and Table S2.5). Given that K is not usually linked to environmental concerns, a main concern might relate to the cost of excess fertilisation. Newfoundland and Labrador dairy farms do produce sufficient manure to likely satisfy the entire K need of farmlands managed by the same dairy farms (Butler et al., 2017).

2.5. Conclusions

Analysis of soil test results could be employed to throw light onto the soil's capacity to receive further P fertilisation and also to point out to possible local inefficiencies in nutrient management. This pose both economic and environmental concerns and thus warrant further investigations that can support greater specificity in fertiliser recommendations. Furthermore, while the age of the fields represented in the farm tests dataset could not be estimated from the available data it is reasonable to speculate that the availability of Al and Fe might have a relationship to the age of land-use conversion, and thus to the speciation of P. This warrants further scrutiny of the utility of soil tests and their interpretation and thus related recommendations, in relation to the age of the land-use conversion. Results suggest that about 12% of the soil tests have Mehlich-3 P above the recommended threshold for environmental protection (200 mg P kg^{-1}), and 14% might have exceeded the soil's capacity to store P. Moreover, two thirds of the soil tests have high and excessive P, with at least a partial possible relationship to management. Based on the recommended environmental limit, a *PSI-1* threshold of 0.14 was determined as reasonable for prevention of P loss. While recommendations do not recommend further P fertilisation of soils that have a high P-test results, these do not account for manure P application which is applied to meet N recommendations. One may speculate that such mismatch is more common for farms where manure is readily available. The *legume forage* and also the *mixed forage,* which contains a legume, receive lower N recommendations than for the *grass forage*. This likely also indirectly limits the addition of manure P; consequently, a large proportion of

mixed forage (94% of SPSC>0) and all *legume forage* fields do still have storage capacity for P.

Furthermore, while P and K fertilisation in the province of NL is based on soil tests, N fertilisation is based solely on crop type. In the absence of detailed yield records the assumed yield for nutrient recommendation is an average yield across all regions. The absence of a correlation between the estimated total mineralizable N and N recommendations suggest that there is the potential for a mismatch between plant uptake and available N in the soil. The lime and K recommendations were well correlated to the soil pH and K concentrations, respectively.

These results point to the need for a better understanding of the variations in soils across regions and across conversion ages. Yield data-based fertiliser recommendation research is also recommended to account for the full edaphic and climatic regional variabilities for economic production of food and protection of the environment. Overall, this exercise confirms, that while implementation of a recommendation system based on calibrations from similar regions does help limit excessive fertilisation, it also confirms that best nutrient recommendations do require local collection of data and calibration exercises. The latter is particularly true for the unique situation of NL that has Podzol dominated farmlands, and where significant land areas are continuously converted from boreal forest to agriculture.

2.6. References

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2.7. Supplementary Material

Table S2.1. The mean ± standard deviation of lime, nitrogen, phosphate, and potash recommendations by crop groups. Similar letters in the same column indicate the means are not significantly different at p= 0.05.

Crop Groups	Lime	Nitrogen	P_2O_5	K_2O
Corn Silage (n=131)	$1.6\pm2.6^{a,b}$	114.2 ± 9.1^{a}	25.9 ± 42.7^{a}	48.7 ± 53.9^{a}
Cranberry (n=57)	$0.02\pm0.08^{a,b}$	135.0 ± 0^{b}	76.1 ± 49.2^{b}	107.6 ± 26.1^{b}
Grass Forage (n=161)	4.8 ± 5^{c}	162.4 ± 42.7^{c}	$40.2\pm50.3^{a,c}$	72.1 ± 57^{c}
Lawns/Sods (n=60)	$2.8\pm5.8^{a,d}$	148.0 ± 50.1^{d}	124.6 ± 162.5^{d}	$67.8\pm90.6^{a,c}$
Mixed Forage (n=894)	4.8 ± 4.6^{c}	93.6 ± 20.1^{e}	$48.5\pm47.4^{c,e}$	87.7 ± 55.4^{b}
Other Berries (n=37)	$1.5\pm2.8^{a,b,e}$	109.1 ± 37.5^{a}	$30.5\pm58^{a,e}$	33.8 ± 22.6^{a}
Root Vegetables (n=54)	$2.5\pm3.7^{a,e}$	94.4 ± 30.3^{e}	$97.2\pm61.8^{b,f}$	102.3 ± 46.1^{b}
Other Vegetables (n=109)	$3.0\pm5.2^{d,e}$	$138.2\pm45.3^{b,d}$	$113.3\pm95^{d,f}$	$85.2\pm53^{b,c}$

Table S2.2. The mean ± standard deviation of lime, nitrogen, phosphate, and potash recommendations for mixed forage by regions. Similar letters in the same column indicate the means are not significantly different at p= 0.05.

Nfld Regions	Lime	Nitrogen	P_2O_5	K_2O
East (n=88)	6.9 ± 5.9^{a}	78.2 ± 34.2^{a}	74.3 ± 61.9^{a}	115.6 ± 68.1^{a}
Central (n=30)	3.6 ± 4.4^{b}	58.6 ± 30.6^{b}	89.3 ± 47.6^{a}	122.5 ± 49.4^{a}
Central North (n=57)	6.4 ± 7.2^{a}	81.1 ± 30.2^{a}	51.1 ± 54.9^{b}	75.4 ± 63.5^{b}
West (n=717)	4.4 ± 4.0^{b}	97.9 ± 11.9^{c}	43.4 ± 42.7^{b}	83.8 ± 51.7^{b}

Table S2.3. Preason correlation between soil test variables for all crops.

Variables	pH	OM	CEC	S	Na	Mn	P	K	Fe	Mg	Al	Ca	PSI-1	PSI-2	N in SOM	Soil N:P	BS
Cu	.178**	.306**	.233**	.313**	.408**	0.008	.143**	.256**	-0.031	.219**	-.194**	.304**	.145**	.149**	.306**	-.165**	.265**
Zn	.193**	.280**	.335**	.368**	.240**	0.023	.490**	.137**	.264**	.269**	-.428**	.491**	.565**	.564**	.280**	-.144**	.326**
pH	1	-.138**	.219**	.451**	-0.006	.157**	.364**	.358**	-.303**	.514**	-.258**	.656**	.325**	.341**	-.138**	-.316**	.816**
OM	-.138**	1	.378**	.212**	.407**	-0.017	0.047	.073*	0.056	.197**	-.230**	.214**	.159**	.146**	1.000**	.056*	-0.012
CEC	.219**	.378**	1	.615**	.338**	0.014	.274**	.259**	.135**	.534**	-.165**	.629**	.301**	.305**	.378**	-.145**	.097**
S	.451**	.212**	.615**	1	.296**	.077**	.315**	.319**	0.054	.449**	-.250**	.628**	.315**	.324**	.212**	-.219**	.388**
Na	-0.006	.407**	.338**	.296**	1	0.047	.098**	.339**	.126**	.340**	-.259**	.230**	.170**	.165**	.407**	-.103**	.154**
Mn	.157**	-0.017	0.014	.077**	0.047	1	.141**	.112**	-0.029	0.035	-.202**	.210**	.141**	.144**	-0.017	-.116**	.226**
P	.364**	0.047	.274**	.315**	.098**	.141**	1	.495**	0.019	.122**	-.246**	.585**	.941**	.962**	0.047	-.211**	.413**
K	.358**	.073*	.259**	.319**	.339**	.112**	.495**	1	-.171**	.285**	-.071*	.365**	.425**	.450**	.073*	-.173**	.371**
Fe	-.303**	0.056	.135**	0.054	.126**	-0.029	0.019	-.171**	1	.171**	-.320**	-.119**	.082**	0.042	0.056	0.008	-.169**
Mg	.514**	.197**	.534**	.449**	.340**	0.035	.122**	.285**	.171**	1	-.404**	.440**	.178**	.167**	.197**	-.216**	.541**
Al	-.258**	-.230**	-.165**	-.250**	-.259**	-.202**	-.246**	-.071*	-.320**	-.404**	1	-.397**	-.421**	-.383**	-.230**	.206**	-.449**
Ca	.656**	.214**	.629**	.628**	.230**	.210**	.585**	.365**	-.119**	.440**	-.397**	1	.585**	.603**	.214**	-.293**	.718**
PSI-1	.325**	.159**	.301**	.315**	.170**	.141**	.941**	.425**	.082**	.178**	-.421**	.585**	1	.994**	.159**	-.187**	.405**
PSI-2	.341**	.146**	.305**	.324**	.165**	.144**	.962**	.450**	0.042	.167**	-.383**	.603**	.994**	1	.146**	-.191**	.415**
N in SOM	-.138**	1.000**	.378**	.212**	.407**	-0.017	0.047	.073*	0.056	.197**	-.230**	.214**	.159**	.146**	1	.056*	-0.012
Soil N:P	-.316**	.056*	-.145**	-.219**	-.103**	-.116**	-.211**	-.173**	0.008	-.216**	.206**	-.293**	-.187**	-.191**	.056*	1	-.357**
BS	.816**	-0.012	.097**	.388**	.154**	.226**	.413**	.371**	-.169**	.541**	-.449**	.718**	.405**	.415**	-0.012	-.357**	1
AS	-.322**	-.346**	-.751**	-.534**	-.357**	-.132**	-.264**	-.214**	-.300**	-.602**	.678**	-.599**	-.370**	-.349**	-.346**	.266**	-.339**

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

c Listwise N=1225

Table S2.4. Preason correlation between soil test variables for mixed forage.

Variables	pH	OM	CEC	S	Na	Mn	P	K	Fe	Mg	Al	Ca	PSI-1	PSI-2	N in SOM	Soil N:P	BS
Cu	.235**	.304**	.164**	.318**	.502**	0.055	.387**	.401**	-0.058	.226**	-.237**	.407**	.341**	.371**	.304**	-.179**	.363**
Zn	.182**	.257**	.156**	.276**	.245**	-0.05	.532**	0.04	.449**	.345**	-.489**	.370**	.605**	.591**	.257**	-.154**	.348**
pH	1	-.101**	.246**	.460**	.075*	.148**	.281**	.299**	-.255**	.585**	-.298**	.697**	.260**	.279**	-.101**	-.357**	.773**
OM	-.101**	1	.242**	.108**	.347**	-0.037	.152**	.219**	.082*	.154**	-.266**	.182**	.278**	.263**	1.000**	0.045	0.043
CEC	.246**	.242**	1	.556**	.273**	-0.054	.101**	.264**	.152**	.595**	-0.055	.560**	.098**	.100**	.242**	-.181**	0.042
S	.460**	.108**	.556**	1	.239**	0.057	.277**	.285**	.154**	.490**	-.237**	.555**	.240**	.251**	.108**	-.233**	.321**
Na	.075*	.347**	.273**	.239**	1	.128**	.235**	.396**	.161**	.304**	-.229**	.287**	.253**	.259**	.347**	-.128**	.226**
Mn	.148**	-0.037	-0.054	0.057	.128**	1	.138**	.140**	-.087*	0.051	-0.063	.118**	.091**	.114**	-0.037	-.142**	.194**
P	.281**	.152**	.101**	.277**	.235**	.138**	1	.249**	.113**	.182**	-.389**	.467**	.887**	.934**	.152**	-.286**	.420**
K	.299**	.219**	.264**	.285**	.396**	.140**	.249**	1	-.211**	.293**	-0.007	.332**	.169**	.205**	.219**	-.169**	.304**
Fe	-.255**	.082*	.152**	.154**	.161**	-.087*	.113**	-.211**	1	.212**	-.346**	-0.05	.220**	.168**	.082*	0	-.091**
Mg	.585**	.154**	.595**	.490**	.304**	0.051	.182**	.293**	.212**	1	-.412**	.650**	.255**	.242**	.154**	-.278**	.623**
Al	-.298**	-.266**	-0.055	-.237**	-.229**	-0.063	-.389**	-0.007	-.346**	-.412**	1	-.435**	-.628**	-.588**	-.266**	.203**	-.497**
Ca	.697**	.182**	.560**	.555**	.287**	.118**	.467**	.332**	-0.05	.650**	-.435**	1	.444**	.469**	.182**	-.345**	.763**
PSI-1	.260**	.278**	.098**	.240**	.253**	.091**	.887**	.169**	.220**	.255**	-.628**	.444**	1	.991**	.278**	-.239**	.425**
PSI-2	.279**	.263**	.100**	.251**	.259**	.114**	.934**	.205**	.168**	.242**	-.588**	.469**	.991**	1	.263**	-.254**	.441**
N in SOM	-.101**	1.000**	.242**	.108**	.347**	-0.037	.152**	.219**	.082*	.154**	-.266**	.182**	.278**	.263**	1	0.045	0.043
Soil N:P	-.357**	0.045	-.181**	-.233**	-.128**	-.142**	-.286**	-.169**	0	-.278**	.203**	-.345**	-.239**	-.254**	0.045	1	-.381**
BS	.773**	0.043	0.042	.321**	.226**	.194**	.420**	.304**	-.091**	.623**	-.497**	.763**	.425**	.441**	0.043	-.381**	1
AS	-.397**	-.323**	-.735**	-.516**	-.338**	-0.015	-.317**	-.207**	-.316**	-.687**	.643**	-.645**	-.455**	-.432**	-.323**	.356**	-.368**

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

c Listwise N=809

Table S2.5. Pearson correlation of lime, nitrogen, phosphate, and potash recommendations for all crops pooled together, mixed forage, and cranberry with soil test variables. Not applicable (na).

	Lime recommendation			Nitrogen recommendations			P_2O_5 recommendations			K_2O recommendations		
Variables	All Crops	Mixed Forage	Cranberry	All Crops	Mixed Forage	Cranberry	All Crops	Mixed Forage	Cranberry	All Crops	Mixed Forage	Cranberry
B	-0.03	-0.04	-0.1	0.04	0.03	na	-0.05	0.02	-0.22	-0.07**	0	-0.74**
Cu	-0.17	-0.24**	-0.25	0.09**	0.14**	na	-0.41**	-0.42**	-0.18	-0.36**	-0.35**	-0.82**
Zn	-0.21**	-0.24**	-0.24	0.10**	0.10**	na	-0.35**	-0.41**	-0.45**	-0.17**	-0.03	-0.69**
pH	-0.82**	-0.85**	-0.35*	0.13**	0.19**	na	-0.39**	-0.39**	0.06	-0.33**	-0.24**	-0.84**
SOM	0.08**	0.08*	na	0.03	-0.03	na	-0.04	-0.06	na	-0.11**	-0.20**	na
CEC	-0.02	-0.04	-0.08	0.00	0.15**	na	-0.29**	-0.15**	0.08	-0.35**	-0.33**	-0.78**
S	-0.32**	-0.34**	-0.12	0.00	0.120*	na	-0.38**	-0.32**	-0.16	-0.36**	-0.27**	-0.73**
Na	-0.06*	-0.11**	-0.02	-0.01	0.20**	na	-0.17**	-0.24**	0.18	-0.23**	-0.30**	-0.05
Mn	-0.22**	-0.16**	-0.29	0.06*	0.06	na	-0.06*	-0.14**	0.1	-0.08**	-0.01	-0.92**
P	-0.30**	-0.35**	-0.09	0.20**	0.16**	na	-0.40**	-0.72**	-0.95**	-0.35**	-0.20**	-0.13
K	-0.23**	-0.22**	-0.26	0.09**	0.07*	na	-0.33**	-0.26**	-0.04	-0.75**	-0.83**	-0.99**
Fe	0.22**	0.20**	-0.11	0.01	0.14**	na	-0.17**	-0.14**	-0.18	0.07**	0.16**	-0.74**
Mg	-0.35**	-.05**	-0.41**	0.02	0.25**	na	-0.28**	-0.33**	0.18	-0.34**	-0.39**	-0.57**
Al	0.33**	0.45**	0.48**	-0.15**	-0.25**	na	0.01	0.47**	0.15	-0.05*	-0.01	0.73**
Ca	-0.58**	-0.67**	-0.25	0.16**	0.25**	na	-0.40**	-0.49**	-0.04	-0.34**	-0.23**	-0.90**
PSI_1	-0.27**	-0.34**	-0.12	0.22**	0.15**	na	-0.18**	-0.65**	-0.56**	-0.18**	-0.13**	-0.25
PSI_2	-0.31**	-0.35**	-0.15	0.23**	0.15**	na	-0.28**	-0.68**	-0.64**	-0.26**	-0.160**	-0.32*
N	0.14**	0.07*	na	-0.06*	0.07*	na	-0.22**	-0.094*	na	-0.21**	-0.20**	na
Soil N:P	0.33**	0.33**	na	-0.12**	-0.32**	na	0.28**	0.43**	na	0.17**	0.18**	na
BS	-0.79**	-0.83**	-0.40*	0.18**	0.27**	na	-0.38**	-0.52*	-0.05	-0.31**	-0.23**	-0.58**
AS	-0.01	0.22**	-0.01	0.02	-0.26**	na	0.07**	0.38**	0.08	0.09**	0.24**	0.36*

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table S2.6. Tests of between-subjects effects from the analysis general linear model univariate.

Tests of Between-Subjects Effects

Dependent Variable: pH

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	266.857a	98	2.723	11.138	0.00
Intercept	5996.057	1	5996.057	24524.7	0.00
Crop_Group	13.917	7	1.988	8.132	0.00
Region	9.328	3	3.109	12.718	0.00
Sample_Year	**0.545**	**3**	**0.182**	**0.743**	**0.53**
Sample_Season	5.862	2	2.931	11.988	0.00
Crop_Group * Region	25.234	9	2.804	11.468	0.00
Crop_Group * Sample_Year	9.622	16	0.601	2.46	0.00
Crop_Group * Sample_Season	12.06	9	1.34	5.481	0.00
Region * Sample_Year	13.38	9	1.487	6.081	0.00
Region * Sample_Season	**0.82**	**2**	**0.41**	**1.676**	**0.19**
Sample_Year * Sample_Season	6.858	6	1.143	4.675	0.00
Crop_Group * Region * Sample_Year	10.644	2	5.322	21.768	0.00
Crop_Group * Sample_Year * Sample_Season	**0.539**	**3**	**0.18**	**0.734**	**0.53**
Error	343.265	1404	0.244		
Total	54938.31	1503			
Corrected Total	610.122	1502			

a R Squared = 0.437 (Adjusted R Squared = 0.398)

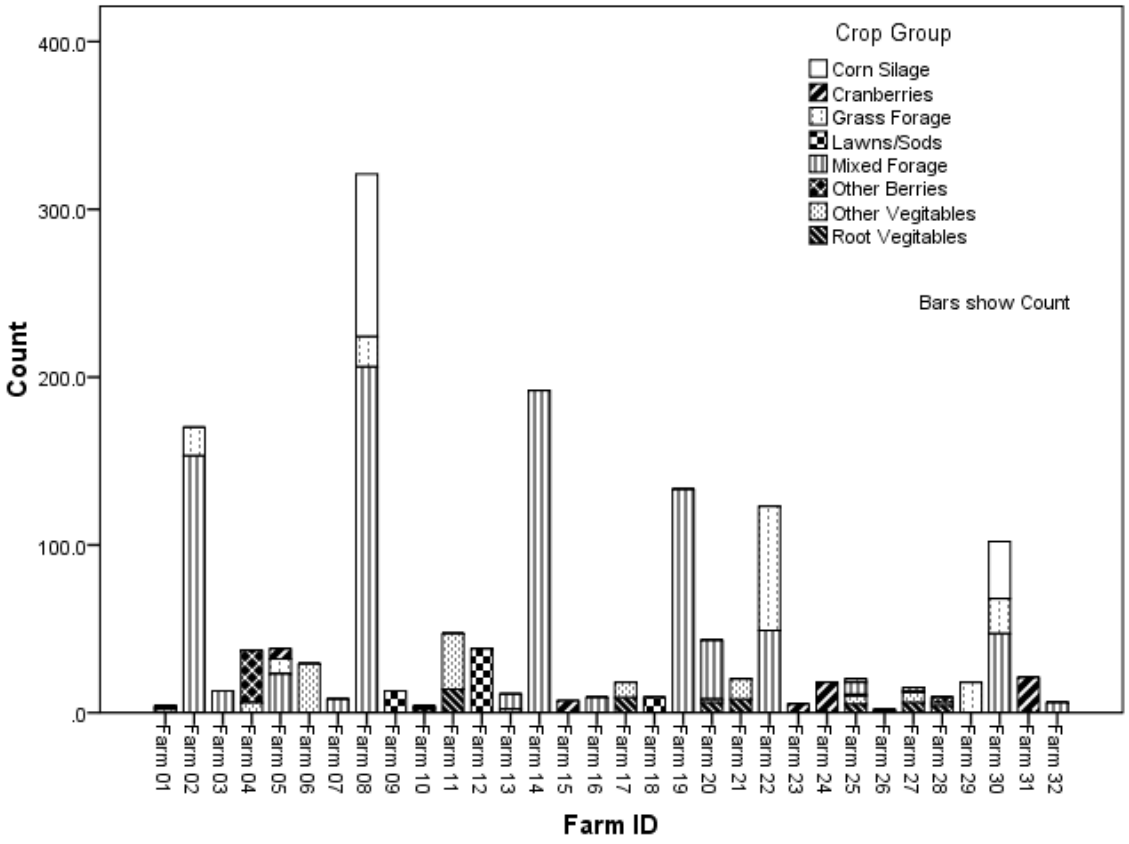


Figure S2.1. Distribution of crop groups by farm ID.

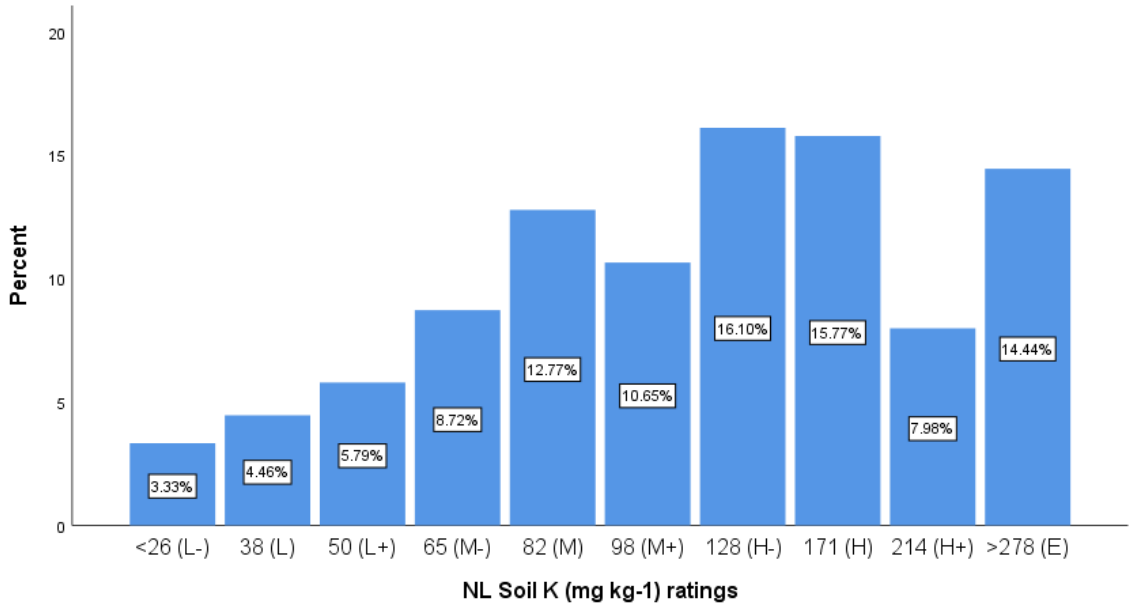


Figure S2.2. Soil K (mg kg^{-1}) ratings for general field crops used by the Newfoundland and Labrador Department of Fisheries and Land Resources (adopted from Nova Scotia Department of Agriculture and Fisheries, September 2008).

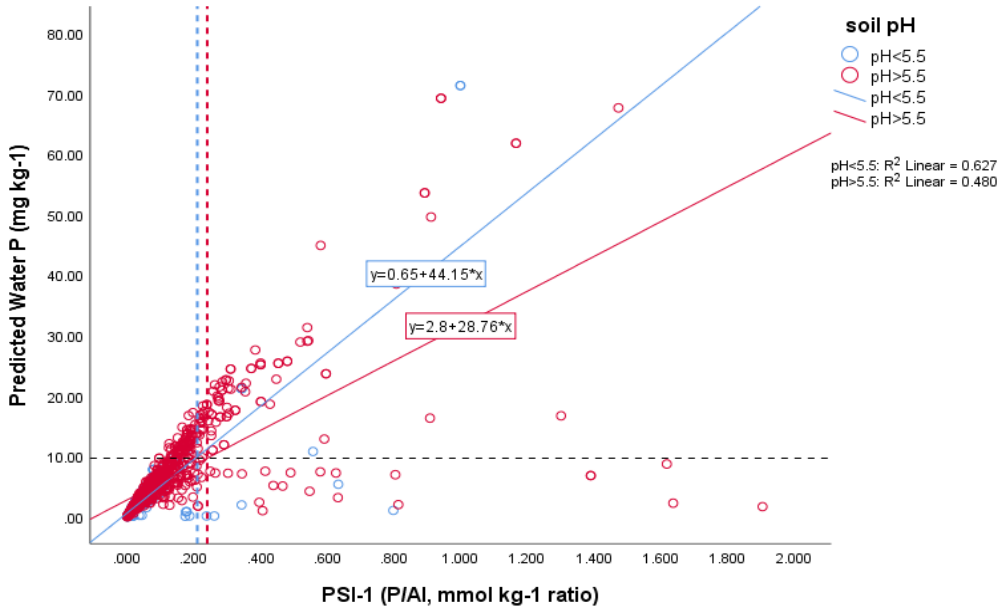


Figure S2.3. Correlation between predicted water-extractable P (water-P = 0.048*Mehlich-3 P, R^2 = 0.45 from chapter 3 P test comparison experiment) and phosphorus saturation index (PSI=P/Al, mmol kg^{-1} ratio) grouped by soil pH.

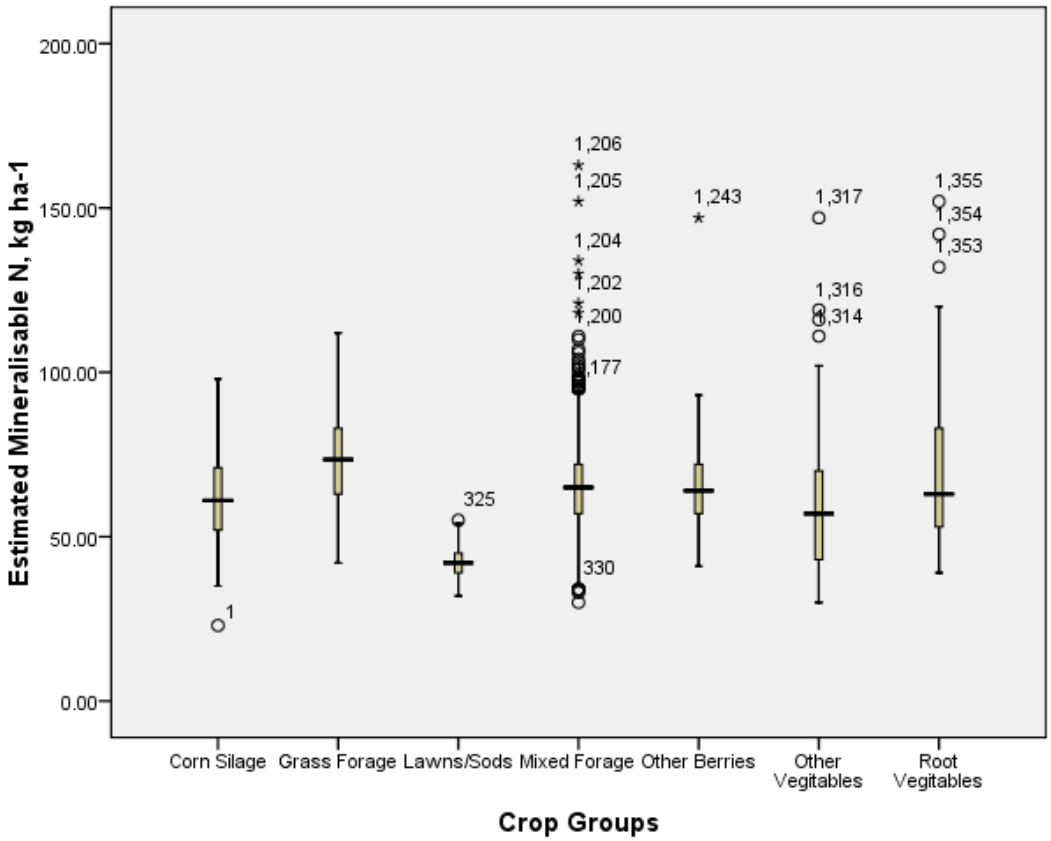


Figure S2.4. Distribution of estimated mineralizable N from SOM by crop groups.

Chapter 3. A COMPARISON OF AGRI-ENVIRONMENTAL PHOSPHORUS TESTS FOR AGRICULTURAL AND NATURAL PODZOLS

3.1. Abstract

Dozens of soil extraction methods for phosphorus tests (P-*tests*) have been developed to quantify P in the soil for agri-environmental benefits. The expansion of agriculture into northern regions dominated by Podzols requires further insights into understanding P extractability for sustainable P management. Hence, this study compared the P extractability from Podzol using ten soil P-*tests*. P in extracts was measured by both colorimetry and inductively coupled plasma mass spectroscopy (ICP-MS). Ninety-six soil samples were collected by depth and horizon from agricultural fields and forest or natural grasslands at three locations with distinct management histories across Newfoundland, Canada. Results show that soil P measurements were statistically similar for Mehlich-3, Bray-1, and Olsen extractions. Colorimetric measurements allowed for better correlations between the P values obtained with various P-*tests*. Nevertheless, for the Mehlich-3 extracts, both measurement techniques produced comparable results. Furthermore, measured soil parameters were employed in multiple linear regressions to predict the P extracted with water, citric acid, Olsen, Mehlich-1, Bray-1, Bray-2 or Mehlich-3. While regression fits ranged from 0.52 for water *test* to 0.95 for Bray-1 *test*, there was no consistency in best predictive soil parameters across *P-tests*. Even though better

correlations were found between the P-*test*s, I recommend calibrating the *tests* with crop yield or P uptake by the plant in the Nfld Podzols for sustainable P management.

Key words: agri-environmental, soil phosphorus test, spectrophotometry, ICP-MS, Podzol

3.2. Introduction

Phosphorus (P) is vital for all forms of life and thus essential for food production (Cordell & White, 2013; Elser & Bennett, 2011). Incentivized by the Green Revolution, accelerated use of P by agriculture is central to feeding the increasing population (IFPRI, 2002). Commonly, P is supplied to crops either as chemical fertilizer or as a component of organic materials such as livestock manures (Jianbo et al., 2011). P availability to plant roots depends on the P source, concentration and chemical form, soil pH, the mineral profile of the soil and the root structure (Baker and Eimers, 2015; Eriksson et al., 2015; Evans, 1988; Kochian, 2012). However, its limited mobility and availability to crops once in soils led to repetitive and excessive application of P in agricultural fields. This resulted in gradual accumulation of P in the soil (Zhu et al., 2017; Luo et al., 2017; Sharpley et al., 2014). One easily discernible effect of this is the risk for delivery of P through erosion (Hart et al., 2004), primarily, but also, under the right chemical conditions (Luo et al., 2017), through leaching to water bodies causing algal blooms (Malley and Watts, 2016; Schindler et al., 2016).

The classical understanding of nutrient availability and nutrient management in the soil is derived from studies conducted on soils traditionally considered of high agricultural value,

i.e., soils with a loamy to fine texture and a near-neutral pH. Expanding agriculture onto other soil types with contrasting edaphic parameters, such as Podzols, requires careful investigation of the determinants of soil fertility. Podzols typically have a coarse-sandy texture and a pH of 4 to 4.5 in the topsoil (Sauer et al., 2007). These conditions signal a poor overall nutrient supply potential for the crops. Moreover, prior studies suggest that nutrient availability in Podzols may not conform to classical tenets of agricultural soil chemistry (Grand & Lavkulich, 2013). Nevertheless, northward expansion of agricultural climate (King et al., 2018) has spurred policy support for agricultural development through conversion of natural lands on Podzols to agricultural use (Government of NL, 2017). As this trend accelerates there is an urgent need to develop the fundamental and applied understanding of P availability in converted Podzols, to ensure that nutrient management techniques may be adapted to allow for environmentally and economically sustainable agricultural production systems.

Since the early 1940s, soil testing, including for P, has been advanced to inform on the status of soil fertility and support nutrient management recommendations (Peck, 1990). Soil tests for P (P-*test*) were developed to gauge the rhizosphere availability of P for different soil types, under the assumption that the tests' results mimic the chemical speciation at the interface between roots and soil (Peck, 1990; Bernardo van Raij, 1998). The decision on selecting a best P-*test* is mainly based on soil's properties, specifically pH (Jones, 2001). There are at least seventeen different extraction methods used to assess P pools thought to be bioavailable in the short- to medium-term, and several more targeting slowly available or unavailable P pools (Buondonno et al., 1992; Harmsen, 2007; Kleinman et al., 2001; Morgan & Mahmoud, 2016; Nawara et al., 2017; Peck, 1990; Wuenscher et

al., 2015). This diversity arises from the fact that methods have been developed for various soil types and for different applications, as it was recognized very early on that no single extractant could give an accurate assessment of plant-accessible P across the range of soil conditions (Rost, 1917; Bernardo van Raij, 1998). Thus, any "new" soil requires careful consideration of the best P-*test*. This study compares the extractability of P in Podzols as measured by P-*tests* commonly employed for agri-environmental purposes. The measured, extractable soil P by the different P-*tests* reflects the chemical species and dynamics of P in soils that may be used for decision making on agronomic and environmental management of P (Adesanwo et al., 2013).

Most soil tests that might be suitable for Podzols have only been evaluated in the context of forest nutrition; it is thus important to test the pertinence of selected methods in an agricultural context. Given the impact of land-use conversion on soil organic matter amounts and types, and on the soil mineralogy in the top layers (i.e., conversion is more representative of deeper layers than for natural Podzols) it is hypothesized that extractability and thus the basis for P fertilizer recommendations will vary as a function of the land-use status. The aims of this study were to: (1) assess ten common extraction methods to determine putative extractability of the soluble reactive (bio-available) and total P as quantified by spectrophotometry (Murphy and Riley ,1962, ascorbic acid method as modified by Watanabe and Olsen (De Silva et al., 2015; Miller & Arai, 2016; Watanabe & Olsen, 1965)) or inductively coupled plasma mass spectroscopy (ICP-MS) (Ivanov et al., 2012), and (2) evaluate the putative relationship between soil properties and P quantified by the said combinations of methods.

3.3. Materials and Methods

3.3.1. Site Description

Soil samples were collected from three locations managed for agricultural and natural grassland or forest from across the island of Newfoundland (*Nfld*), part of the Province of Newfoundland and Labrador (NL), Canada: (1) in November 2017 at the St. John's Research and Development Centre of Agriculture and Agri-Food Canada (*SJRDC*) in eastern Newfoundland (47.56° N, 52.71° W); (2) in August 2017 at the provincial Centre for Agriculture and Forestry Development (*CAFD*), located in Wooddale, central NL (49.03° N, 55.55° W) and (3) in August 2016 from a dairy farm located in Cormack (*Cormack*), western Nfld (49.19° N, 57.24° W).

SJRDC is located at 114 m above sea level (asl); it receives an annual mean rainfall of 1534 mm had an annual mean temperature of 5 °C (Government of Canada, 2019a); The SJRDC *managed* field has been in agriculture for about 150 to 160 years, with a common management including a mix of timothy (*Phleum pratense*), red clover (*Trifolium pratense*) and alsike clover (*Trifolium hybridum*) alternating with research crops. Fields receive variable amounts of mineral fertiliser or manure and are regularly limed (Woodrow et al., 1996, unpublished report). The relatively young *forested SJRDC* soil lacks an E horizon, a residual effect of the relatively recent disturbance (about 25 years ago), which did not allow yet for significant re-podsolization after replantation with black spruce (*Picea mariana*). The *forested* CAFD soil has well-developed podzolic soil horizons (LFH, E, B, BC, and C). *SJRDC* soil is an Orthic Humo Ferric Podzol developed on a glacial till (Heringa, 1981).

The *CAFD* is located 46 m asl with an annual mean rainfall of 1108 mm and an annual mean temperature of 4.4 °C (Government of Canada, 2019a). The CAFD *managed* field was used as a tree nursery for about 30 years with a history of fertiliser application (Government of NL, 2019). *CAFD* soil is a Ferro-Humic Podzols developed on glaciofluvial deposits (Sanborn et al., 2011).

Cormack is at an average altitude of 154 m (asl), with an average annual precipitation of 1264 mm and annual mean temperature of 3.2 °C (Government of Canada, 2019a). The field has been under various annual crop rotations (centred on potato and wheat) since the 1950s. This field receives regularly mineral fertilizers and manure and irregular lime application (personal communication). The site is located on humo-ferric Podzols developed over a loam to sandy loam till originating from shale and soft sandstone parent materials (South, 1983; Government of Canada, 2019b).

For each site, reference soil was collected from the *unmanaged* field next to the *managed* site. Newfoundland and Labrador agriculture occurs exclusively on lands converted from boreal forest to agricultural use, nearly exclusively of Podzols.

3.3.2. Soil Sampling

The soil samples were collected from sites at the *SJRDC* (fields approx. 160 years old), *Cormack* (fields approx. 70 years old), and *CAFD* (fields approx. 5 years old).

SJRDC: 46 soil samples were collected from the 0-20 cm and 20-40 cm soil depths of agriculturally *managed* plots, and 6 soil samples of LFH and B-horizons from adjacent forested area. *Cormack*: 16 soil samples were collected from a *managed* field, with another 8 from the surrounding buffer zones covered with natural grassland; these were collected

at 0-10 cm and 10-20 cm depths (obtained from archived samples, Adrian Unc). *CAFD*: 20 soil samples were collected from the *managed* Ap and E, and the *forested* LFH, E, and B-horizons. Usually, after conversion from forest to agricultural use, the LFH, E and B horizons are mixed during site clearing and preparation, to eventually produce the plough layer (Ap horizon).

Thus, a total of 96 soil samples were obtained to represent three locations, three management types, as well as different soil depths and horizons. The variation in number of samples at each location reflects the diversity in soil conditions at each site. Thus, the soil samples representing three locations, various managements histories, various depths, and several horizons were used in the inventory of *P-test* methods applicable to Nfld soil types.

3.3.3. Soil P Extraction and Analyses

Soil samples were air-dried and passed through a 2 mm sieve before being analyzed for (1) soil organic matter (SOM) based on loss-on-ignition method at 430 °C for 6 h, (2) pH and electrical conductivity (EC) measured in 1:2 soil to double distilled water (DDW) ratio or 1:5 soil to DDW ratio for soils with high organic matter content, (3) particle size distribution determined with hydrometer method (Carter & Gregorich, 2008), (4) exchangeable cations were extracted with Mehlich-3 in a 1:10 soil to solution ratio (Carter & Gregorich, 2008) and (5) different P pools in the soil were extracted by ten soil P extraction methods (Table S3.1, Supplemental Material). The water and 0.01M $CaCl_2$ solution were used to extract readily available P pool while Mehlich-1, Mehlich-3, Olsen, Bray-2, ammonium bicarbonate diethylenetriaminepentaacetic acid (AB), Morgan's and

1% citric acid solutions were used to extract fixed P pools from minerals soils. The description and procedure for each P-tests presented in the supplemental material section and Table S3.1. The soil P extraction of each P-test has been applied as per the references provided in the

Soluble reactive P (srP) or available P was measured with the Murphy and Riley (1962) ascorbic acid method as modified by Watanabe and Olsen (1965) while total P and cations like Al, Fe, potassium (K), and calcium (Ca) were measured by ICP-MS (i-Cap Q, Thermo Scientific™ Burlington ON, Canada). The P concentration in each extract is reported as mg P kg^{-1} dry soil.

3.3.4. Statistical Analysis

Descriptive and explanatory statistics were carried out using SPSS (SPSS Inc, 2017) and OriginPro 2020 (OriginLab Corporation, Northampton, MA, USA). Pearson correlations and principal component analyses (PCA) were employed to illuminate the relationships between the measured soil P and soil properties. The means of the soil P extracted and measured by the various methods were compared using a one-way *ANOVA* followed by a Tukey's posthoc test at the 0.05 significance level; similar variance was assumed.

Furthermore, multiple linear regressions were performed to assess the relationship between soil P as extracted and analysed with the different protocols. The Mehlich-3 method, as the current method officially employed in NL, was used as the predictor variable. Each regression retained the soil parameters that had a statistically significant (<0.05) impact on the model.

3.4. Results and Discussion

3.4.1. Physicochemical Properties of the Studied Soils

The physicochemical characteristics of the studied soils are presented in Table S3.2. The soil texture of the *Cormack* field was classified as clay loam: 20-38% sand, 29-49% silt, and 23-38% clay. The *Cormack managed* soils collected from 0-10 cm and 10-20 cm have a pH of 5.93 ± 0.38 and 5.89 ± 0.35, respectively (Table S3.2). The pH of soil sampled from the natural buffer zone (grassland) next to the *Cormack managed* field, also collected at 0-10 cm and 10-20 cm, has a pH of 6.27 ± 0.08 and 6.07 ± 0.42, respectively (Table S3.2). The pH in the *managed Cormack* soils is slightly lower than forested soils ($p = 0.078$), which could be linked to slightly higher Al concentrations (as measured by the Mehlich-3 method) ($p = 0.017$, Dunn's post hoc test). Additionally, the application of large amounts of manure might enhance the mineralization of organic carbon and nitrogen, which might decreased soil pH (Thomson et al., 1993). The higher Al level in *managed Cormack* field samples might also be due to deep ploughing, which can bring up the amorphous Al silicate or organic Al complex materials, which can also favor fixation of P, and thus reduction of available P, in the plough layer (Ap) (Schnitzer & Desjardins, 1969).

The *managed* soils of *SJRDC* have more silt content (49.59 ± 5.03%), while the *unmanaged* B horizon has more sand content (43.85± 5.03%), which indicates that the long-term management (over approximately 160 years) might have shifted the sandy soil to more silty soil due to the management effects (mechanical effect). Also, the *managed SJRDC* soils have a soil pH of ~6.5 regardless of the soil depth, which is a favorable agronomic pH range. Moreover, the pH of *unmanaged SJRDC* soils from ~5.2 were increased by more

than one pH unit relative to the *managed SJRDC* soils, which is likely related to the long-term management history (cropping, fertilizer, and lime use).

The recently converted and *unmanaged CAFD* soils were more acidic (pH<5.5) and sandy textured (50% sand) compared to the other locations. The converted Ap of the *CAFD managed* field has a lower pH compared to the *Cormack* fields which have been managed since 1950, which further supports the assumption that long-term agricultural management increases the soil pH. Consequently, the lower pH of the *managed CAFD* field might be attributed to its recent conversion from forestry to agriculture, which means not enough acid-neutralizing lime has yet been applied as the sandier soil texture enhanced the acidity driven leaching of acid-neutralizing base cations (Fageria & Nascente, 2014).

The average SOM in *managed Cormack* soils were not significantly different than *unmanaged Cormack* soils, regardless of the depth ($p = 0.85$). The *managed Cormack* field has been receiving manure twice a year (personal communication), which might help to prevent the decline of SOM. But *SJRDC* soils have significantly higher SOM compared to both *Cormack* and *CAFD* soils ($p<0.001$), another parameter that is likely a legacy of the accelerated turnover of SOM and nutrients during the long-term history of agricultural management (Doran et al., 1996; Von Lützow et al., 2002). The SOM of the *managed* fields at the three locations, for all depths, was higher than the critical level of 3.4% SOM (2% C) proposed by the European Soil Strategy Commission for sustainable crop production (Hanegraaf et al., 2009). However, the SOM varies by depth, topography, management, soil texture, and drainage. For example, in the United States' mineral soils, a SOM of up to 6% was reported (Broadbent, 1974). Comparing to the United States' mineral agriculture soils, the recently converted *CAFD managed* Ap soil needs to be improved to sustain the

soil fertility of this specific field (Abedin, 2018; Doran et al., 1996). The relatively lower SOM obtained in the *managed CAFD* Ap horizon can be attributed to the lower SOM (3.24 ± 0.05 %) of unmanaged B horizon (Table S3.2). Thus, the dynamics of SOM in Nfld Podzols are affected by soil formation, geographic locations, weather conditions, and type and duration of management.

The *managed Cormack* soils have slightly higher Al as extracted by Mehlich-3 solution than natural soils ($p = 0.017$, Dunn's post hoc test) while Fe, K, Ca are not significantly different ($p>0.05$). The means of cations mentioned above were significantly different between locations.

3.4.2. Comparison of Spectrophotometrically Measured P-*tests*

P extractable by the water, $CaCl_2$, AB, and Morgan and Mehlich-1, Olsen, Bray-1 and Mehlich-3 were statistically similar ($p>0.05$) whereas citric acid, and Bray-2 methods extracted significantly higher P than other methods ($p<0.05$) (Table S3.3, Supplemental Material and Figure 3.2a). Soil P extractability (grand means, n=96) increased as follows: $CaCl_2 \leq$ water $\leq$ Morgan $\leq$ AB $<$ Mehlich-1 $\leq$ Bray-1 $\leq$ Mehlich-3 $\leq$ Olsen $<<$ Bray-2 $<<<$citric acid (Figure 3.1., Figure 3.2a and Table S3.3). Similar trends were reported in other studies (Kulhánek et al., 2007; Kumaragamage et al., 2007; Maguire & Sims, 2002; Wuenscher et al., 2015) despite the differences in soil types, management, residual soil P, and variations in extraction parameters.

The soil P extracted by water (*water-P*) reflects the readily available P for the plant (Abdu N, 2006) and mobile P concentrations in the soil (Glæsner et al., 2013). Both *water-P* and *$CaCl_2$-P* may be used for environmental protection decisions, as they were previously

correlated with the risk of P leaching (Maguire & Sims, 2002). The subsurface *managed SJRDC* soils (20-40 cm) have mean *water-P* concentrations (13.25 ± 9.45 mg P kg^{-1}) above the recommended environmental critical P level (9.70 mg P Kg^{-1} *water-P*) (Khiari et al., 2000), albeit, given the large error range, not statistically significant. This could be due to the effect of long-term liming favouring P solubilisation and thus P runoff and downward mobility (Cox et al., 2000). Nevertheless, the concentrations of *water-P* were negligible, from an agronomic point of view, for all samples except for the forest floor, which is usually lost during conversion through agriculture. This indicated that in Podzols not receiving limestone amendments the opportunity for passive P uptake by plants is extremely limited (Table S3.3). While, largely, both *water-P* and *$CaCl_2$-P*, indicate minor risks of P loss, same results may nevertheless suggest the reality of long-term vertical P transfer and accumulation into the deeper soil layers of these acidic Podzols, where it can react with accumulated Al and organic carbon favoring accumulation of unavailable P chemical species. (Ohno & Amirbahman, 2010). This is a standard podsolization mechanism that removes P from the available pool.

In comparison to Mehlich-3, the current method used in NL, both the Morgan and AB methods yielded lower available P concentrations; these two methods are nevertheless recommended elsewhere for agronomic use on acid soils. Specifically, the Morgan method is recommended for agri-environmental purposes in Ireland that have acidic soils despite its low efficiency observed in this study (Daly, 2005; Jones, 2001). The lower performance of Morgan in Nfld Podzols might be related to the chemical properties of the soil, and differences in extraction ratios and time (Daly, 2005).

Among the agronomic soil P extraction methods analyzed spectrophotometrically, the 1% citric acid yielded 3 to 50-fold more reactive P (Table S3.3, Supplemental Material). For example, the largest mean soil P concentrations were measured in citric acid extract for the *managed Cormack* (314 ± 87 mg P kg^{-1} at 0-10 cm and 270±116 mg P kg^{-1} at 10-20 cm, n = 8 for each depth) followed by the natural soils from the same area.

The low molecular weight organic acids like citric, oxalic, and malic acid are secreted by plant roots in the soil facilitating the release of P from clay or complexed minerals (Zhu et al., 2017). Similarly, citric acid is believed to extract P attached to both mineral and organic complexes. Previous reports involved 50 soil samples collected from the agriculture fields in Germany and Austria (Wuenscher et al., 2015) have shown higher P extractability with oxalic acid which extracts P bound to ferric and organic complexes. Also, large *citric acid-P* measurements might be due to minimal re-precipitation of the extracted P compared to other agronomic P-*tests* (Penn & Camberato, 2019; Penn et al., 2018).

For long term fertilized calcareous soils it was reported that *citric acid-P* concentrations (2-314 mg P kg^{-1} using 10 mM citric acid; 1:20 soil to solution, 3 h shaking time) are lower than *Mehlich3-P* concentrations (16-1343 mg P kg^{-1}; 1:8 soil to solution) (Jalali & Jalali, 2016, 2017). The reason for lower citric acid extractability of P in calcareous soils is linked to soil properties distinct from acid or neutral soils, but one cannot discount variation of extraction protocol parameters (Jalali & Jalali, 2016). The citric acid method can extract soluble P attached to clay particles and organometallic complexes (DeLuca et al., 2015), a type of P more common in acid soils than in neutral or alkaline soils. The 1% citric acid extraction was recommended for agronomic P budgeting as early as 1894 (Sherrell, 1970; Truog, 1930). However, it is not as widely used as the Olsen and Mehlich-3 methods despite

its confirmed ability to mimic the plant root environment (Darch et al., 2016; Menezes-Blackburn et al., 2016). Further investigations are necessary to establish the relationship with crop yield and environmental quality, especially given the environmentally safe citric acid versus the Mehlich-3 solutions (Benjannet et al., 2018).

On the other hand the Bray-2 method extracted the largest amounts of P (114 ± 14 mg P kg^{-1}) from the *managed CAFD* Ap layer (n=5), and the *managed Cormack* soils (98 ± 14 mg P kg^{-1} and 90 ± 19 mg P kg^{-1} at 0-10 cm and 10-20 cm, respectively) (Table S3.3, Supplemental Material). Thus, *Bray-2-P* was 2 to 3-fold lower than *citric acid-P* but 1.5 to 2-fold above the *Mehlich-3-P*. Similarly, the Bray-2 method extracted more P than the Mehlich-3 method in Louisiana soils (Wang et al., 2004). This could be related to strong acidic Bray-2 solution (has a 4-fold HCl concentration than Bray-1 solution) (Table S3.1, Supplemental Material); in the Nfld soils, it extracted more soil P than all other methods except for the citric acid solution. The Bray-2 solution is designed to extract labile and a portion of nonlabile mineral-bound P (Jones, 2001). Bray-2 method was used for agronomic purposes in NL (until 2013, when the provincial government soil and plant laboratory shifted to Mehlich-3), Australia, New Zealand, Spain, and Greece (Ziadi et al., 2013). In New Zealand, the Bray-2 method has been used to test the available P in acidic soil cultivated with potato and the results were used as the basis for subsequent P recommendations (Sherrell, 1970). Overall, the mean of *Bray-2-P* was significantly greater than for all other methods except citric acid (Figure 3.1.), which mainly reflects the total mineral P in long-term managed and unmanaged mineral soils.

The most widely used agronomic and environmental P-*tests* are Olsen, Mehlich-3, and Bray-1. Surprisingly, there was no significant difference between the mean of soluble P

extracted by these methods (Figure 3.1.a) despite their difference in the P desorption mechanisms. As it was the case for citric acid and Bray-2, these methods extracted more P from *managed Cormack* and *CAFD* soils. It should be noted here that the Olsen method, while it was designed for calcareous soils (Sims & Hodges, 2000; Bernardo van Raij, 1998) has also been used for acidic soils (Kulhánek et al., 2007). The Manitoba agricultural department uses the Olsen method for agronomic and environmental P management (Kumaragamage et al., 2007; Kumaragamage et al., 2011), across a range of soil types. On the other hand, Mehlich-3 is widely used in North America, including NL and the Maritime provinces of Canada. It is also a common extraction protocol elsewhere, employed for both agronomic and environmental P management as it can be employed for multielement extractions alongside P, and the extracts can be conveniently analyzed by ICP (Abdu N, 2006; Jalali & Jalali, 2017; B. Raij, 1994; Szara, Sosulski, Szymańska, & Szyszkowska, 2018). Mehlich-3 method is employed on converted agriculture on acid soils in Nfld despite the lack of a calibration against crop yield.

The comparative evaluation of various P-*tests* versus Mehlich-3 in Podzols of Nfld helped to identify applicable soil P extraction methods. Results show that Mehlich-1, AB, and Morgan methods are not suitable candidates for the tested Podzols, with the opposite being true for Mehlich-3, Olsen, and Bray-1 (Table S3.3, Supplemental Material) agri-environmental P-*tests*.

Table 3.1. Pearson correlation between selected soil properties and P-*tests analysed spectrophotometrically (Colorimetric, Col) or by ICP-MS. The bold values indicate significant correlations ($p<0.05$). Cations were extracted by Mehlich-3 and analyzed by ICP-MS. The P analysis method bracketed after the P-tests.*

P-tests (Analysis)	Al	Fe	K	Ca	pH	EC	SOM	Sand	Clay	Silt
	mg kg^{-1}							**(%)**		
Water P $_{Col}$	0.14	**-0.36**	0.20	**0.63**	**-0.24**	**0.69**	-0.13	-0.20	**0.36**	**-0.24**
$CaCl_2$ P $_{Col}$	0.01	-0.08	**0.32**	**0.38**	0.03	**0.39**	-0.07	-0.20	0.18	-0.01
Citric acid P $_{Col}$	0.09	**-0.39**	**0.31**	**0.61**	**-0.23**	**0.35**	**-0.26**	-0.22	**0.50**	**-0.34**
Olsen P $_{Col}$	-0.07	**-0.29**	**0.36**	**0.57**	-0.13	**0.31**	-0.11	-0.21	**0.38**	-0.22
AB P $_{Col}$	0.13	**-0.35**	-0.04	**0.34**	**-0.25**	**0.28**	-0.12	-0.21	**0.44**	**-0.27**
Morgan P $_{Col}$	**-0.31**	**0.29**	**0.63**	0.15	0.19	**0.44**	0.16	-0.21	-0.07	**0.30**
Bray-1 P $_{Col}$	0.02	**-0.45**	**0.25**	**0.66**	**-0.34**	**0.37**	**-0.27**	**-0.30**	**0.58**	**-0.34**
Bray-2 P $_{Col}$	-0.17	-0.19	**0.49**	**0.45**	-0.10	**0.45**	-0.07	-0.16	**0.28**	-0.16
Mehlich-1 P $_{Col}$	0.17	**-0.49**	0.13	**0.61**	**-0.41**	0.16	**-0.38**	-0.22	**0.59**	**-0.45**
Mehlich-3 P $_{Col}$	-0.02	**-0.38**	**0.36**	**0.70**	-0.19	**0.48**	-0.21	**-0.29**	**0.52**	**-0.28**
Water P $_{ICP}$	**-0.26**	**0.10**	**0.49**	**0.26**	-0.06	**0.60**	**0.31**	-0.16	-0.04	0.21
Citric acid P $_{ICP}$	0.13	**-0.34**	**0.28**	**0.44**	**-0.34**	**0.44**	-0.22	-0.15	**0.42**	**-0.31**
AB P $_{ICP}$	**-0.27**	**0.58**	**0.59**	**-0.31**	-0.13	**0.38**	**0.59**	0.15	**-0.53**	**0.40**
Morgan P $_{ICP}$	**-0.34**	**0.44**	**0.72**	**-0.01**	-0.01	**0.54**	**0.45**	-0.01	**-0.31**	**0.36**
Bray-1 P $_{ICP}$	0.08	**-0.29**	**0.32**	**0.46**	**-0.40**	**0.31**	-0.08	-0.17	**0.35**	-0.21
Bray-2 P $_{ICP}$)	0.01	**-0.22**	**0.41**	**0.43**	**-0.26**	**0.37**	-0.08	-0.12	**0.29**	-0.20
Mehlich-1 P $_{ICP}$	0.11	**-0.44**	**0.09**	**0.49**	**-0.30**	**0.19**	**-0.31**	**-0.28**	**0.61**	**-0.39**
Mehlich-3 P $_{ICP}$	-0.08	**-0.31**	**0.43**	**0.72**	-0.19	**0.50**	-0.12	**-0.25**	**0.43**	-0.21

Table 3.2. Pearson correlation between P-tests analysed spectrophotometrically (Col) or by ICP-MS. The bold values in the cells shows a significant correlation($p<0.05$).

	P analysed spectrophotometrically								
P-tests	Water P	$CaCl_2$ P	Citric acid P	Olsen P	AB P	Morgan P	Bray-1 P	Bray-2 P	Mehlich-1 P
$CaCl_2$ P	**0.50**								
Citric acid P	**0.61**	**0.52**							
Olsen P	**0.47**	**0.34**	**0.84**						
AB P	**0.47**	0.16	**0.50**	**0.41**					
Morgan P	**0.24**	**0.38**	**0.45**	**0.27**	**0.61**				
Bray-1 P	**0.62**	**0.43**	**0.91**	**0.77**	**0.47**	**0.31**			
Bray-2 P	**0.48**	**0.41**	**0.86**	**0.77**	**0.30**	**0.50**	**0.83**		
Mehlich-1 P	**0.59**	**0.34**	**0.85**	**0.72**	**0.60**	**0.23**	**0.88**	**0.72**	
Mehlich-3 P	**0.73**	**0.54**	**0.95**	**0.80**	**0.49**	**0.46**	**0.96**	**0.85**	**0.92**
	P analysed by ICP-MS								
	Water	$CaCl_2$	Citric acid	Olsen	AB	Morgan	Bray-1	Bray-2	Mehlich-1
Water P	1.00								
Citric acid P	**0.36**	na	1.00						
AB P	**0.63**	na	0.20	na	1.00				
Morgan P	**0.61**	na	**0.35**	na	**0.81**	1.00			
Bray-1 P	**0.67**	na	**0.67**	na	**0.37**	**0.42**	1.00		
Bray-2 P	**0.63**	na	**0.76**	na	**0.41**	**0.52**	**0.93**	1.00	
Mehlich-1 P	**0.39**	na	**0.64**	na	-0.01	0.10	**0.68**	**0.72**	1.00
Mehlich-3	**0.52**	na	**0.74**	na	0.19	**0.41**	**0.84**	**0.86**	**0.73**

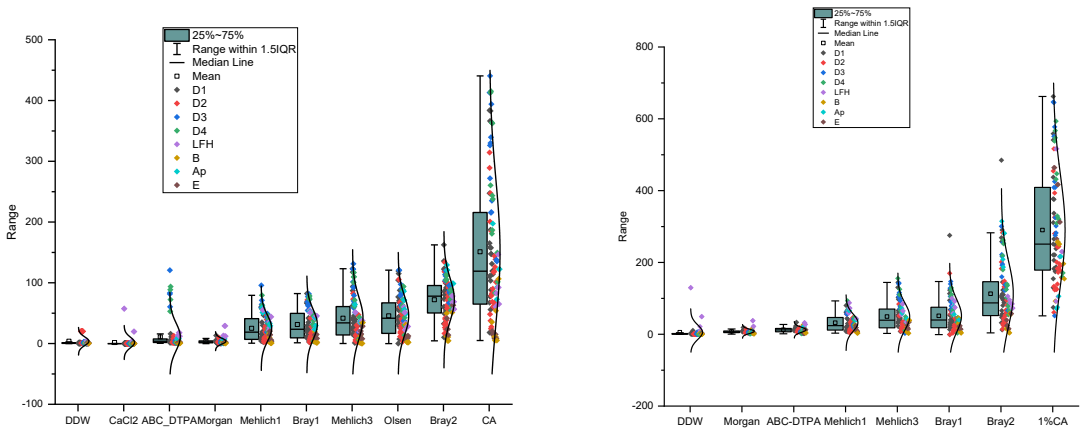
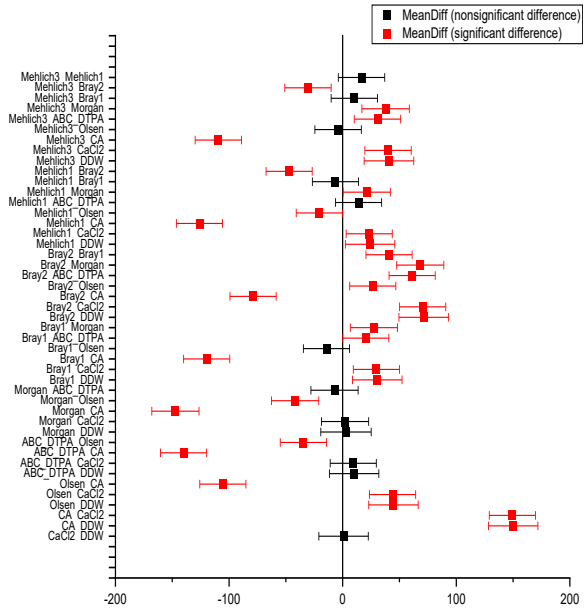


Figure 3.1. Box plots of 10 Soil P extraction methods analyzed (a) spectrophotometrically or by (b) ICP-MS in soil collected by depths and horizons (D1:0-20 cm, D2: 20-40 cm, D3: 0-10 cm, D4: 10-20 cm, and LFH, B, Ap and E are horizons). The unit of all variables is mg P kg^{-1}.

(a)



(b)

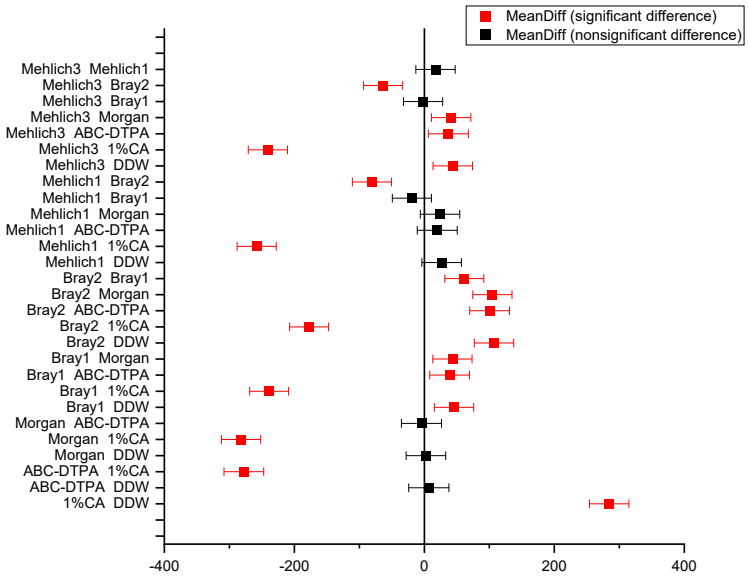


Figure 3.2. One-way ANOVA means comparison plot of 10 P*-tests analyzed (a) spectrophotometrically or by (b)ICP-MS (Tukey test, p = 0.05).*

3.4.3. Comparison of ICP-MS Measured P-*tests*

The ICP-MS measures higher P concentrations than the spectrophotometric analysis in the same soil extract due to its ability to also measure total P available in the extract. The P extractability varies by method types, soil types, and extraction parameters. ICP-MS was used to analyse the extract of eight methods. Two methods, $CaCl_2$ and Olsen, were not analyzed by ICP-MS due to high salt and carbonate content, which interfered with the calibration curves for P, Al, Fe, and K, an exclusion based on preliminary investigations.

Water extracted widely variable amounts of soil P across location, management, and depth/horizons. The highest *water-P* concentrations (89 ± 47 mg P kg^{-1}) were observed for the *forested* LFH horizon of *CAFD* while no P was detected for the *managed CAFD* E horizon. This could be due, at least partly, to the capability of the ICP-MS to oxidize organic P in soils with high SOM (Ivanov et al., 2012).

The *Morgan-P* and *AB-P* measured by ICP-MS had trends similar to the ones measured by spectrophotometry. Originally, AB was developed as a universal extractant for multiple elements (Raij, 1994; Soltanpour, 1985), and it was reported to correlate well with the Olsen method (Jones, 2001). The low extractability observed for the AB and Morgan methods suggests they are not suitable for the tested Podzols.

Also, the ICP-MS measurements for Bray-1 and Mehlich-3 extracts (Table S3.4, Supplemental Material and Figure 3.1b) are similar to *Bray-1-P* and *Mehlich-3-P* analyzed by spectrophotometry. The means of extracted soil P measured by ICP-MS by the eight *P-tests* increased in the following order: water ≤ Morgan ≤ AB ≤ Mehlich-1 ≤ Mehlich-3 ≤ Bray-1 << Bray-2 <<< citric acid (Table S3.4, Supplemental Material and Figure 3.2b).

Furthermore, the soil P extractability by these methods grouped into four categories, with concentrations statistically similar within each: (1) water, Morgan, and AB; (2) Mehlich-1, Mehlich-3, and Bray-1; (3) Bray-2; and (4) citric acid. There was no significant difference between the mean of soil P extracted by the P-*tests* 1st and 2nd categories (Table S3.4, Supplemental Material and Figure 3.2b). Exceptionally, the means of *water-P* and *Mehlich-1-P* were statistically similar (p=0.13), an artefact attributable to the very high *water-P* in the unmanaged soils. Mehlich-1 test is generally known to extract more mineral P in the soil than water. Water, Morgan, and AB *tests* might reflect the total P, a parameter informative for environmental protection while Mehlich-1, Mehlich-3, and Bray-1 *tests* can be used for agronomic purposes in these acidic podzolic soils. Bray-2 and citric acid might be proposed to measure more of the total P (a portion of organic and inorganic P) extracted from the soils with natural or legacy P (ref). Moreover, the citric acid solution is able to extract 46-79% of hydrolysable organic P, which is significantly more than Olsen *test*, which only extracts <10% of hydrolysable organic P in the soil (Darch et al., 2016; Hayes et al., 2000). As the citric acid solution might resemble the acids in plant's root exudates, it might be an important target for further evaluations of its applicability to Podzols. Both spectrophotometrical and ICP-MS analyses helped to identify or group the P-*tests* suitable for Nfld managed and unmanaged Podzols with distinctive management and weather conditions. However, further investigation is needed to establish the relationship between P-*test* and crop yield responses.

3.4.4. Relationship Between the P Measurements and Soil Properties

Almost all extraction methods were positively correlated with EC regardless of analytical protocol; however, EC was only available for *managed SJRDC* (n=46) (Table 3.1). Soil Ca concentration was also positively correlated with the P extracted by most of the methods but negatively correlated with AB-P (r =0.31). Furthermore, the *Morgan-P* was not affected by the level of Ca in the soil, as observed from the non-significant correlations for both measurement methods ($p>0.05$). A similar trend was seen for soil K except for water-P, AB-P and Mehlich-1-P analyzed with colorimetry and AB-P methods analyzed with ICP-MS (Table 3.1). Surprisingly, soil Al did not have a significant correlation with the P extracted by most methods regardless of the analysis method; it was nevertheless negatively related with the *Morgan-P* as analysed by both methods, and *water-P* and *AB-P* analysed by ICP-MS. Soil Fe levels were negatively correlated with P obtained by all tests except for Morgan for both analysis methods, and the AB extracts analysed by ICP (Table 3.1). While the cation concentrations were only analysed in Mehlich-3 extracts and thus this might affect some of the correlation tests, *Mehlich-3-Al* was not correlated with *Mehlich-3-P* for both analysis methods.

Clay content was positively correlated with most *P-tests* measurements for most protocols with the exception of AB-P, and Morgan-P analyzed by ICP-MS (Table 3.1). This could be due to the poor P extraction performance observed for both these methods. On the other hand, soil pH and silt content have an inverse relationship with the spectrophotometrically measured *water-P*, *citric-P*, *AB-P*, *Bray-1-P*, and *Mehlich-1-P* (Table 3.1). The non-significant relationship between soil pH with *Mehlich-3-P* and *Olsen-P* confirms their

applicability to both calcareous and non-calcareous soils as a universal extractants. However, for sustainable nutrient management, the recommendation of these methods must be supported with P uptake studies conducted on local soil type and environmental conditions.

In the literature, the relation between soil properties and soil P measured by various extraction methods is not consistent due to the soil variation and aim of the studies (Adesanwo et al., 2013; Darch et al., 2016). However, it was reported that cations like Al and Fe, soil pH, SOM, and soil texture are the major soil properties that affect the soil P extractability by different methods (Abdu N, 2006). Hence, some of the soil properties can be used as surrogate variables to establish a relation between extraction methods analyzed with colorimetry or ICP-MS.

3.4.5. Relationship Between Agri-Environmental P-*Tests*

The soils collected by horizons were excluded due to their lower relevance for agronomic purposes. The environmental P-*tests*, i.e., *water-P* and *$CaCl_2$-P*, analyzed with the colorimetric method, have a significant positive correlation with all agronomic P-*tests*. Specifically, colorimetric *water-P* was strongly correlated with colorimetric *Mehlich-3-P* ($r = 0.73$), *Bray-1-P* ($r = 0.62$), and *citric-P* ($r = 0.61$) Table 3.2. Also, all agronomic P-*tests* analyzed with ICP-MS were significantly correlated with *water-P* analyzed with ICP-MS ($p<0.05$) (Table 3.3). However, *water-P* has a relatively weaker correlation with *Mehlich-3-P* ($r = 0.52$) and *citric-P* ($r = 0.36$) than when analyzed with the colorimetric method. On the other hand, the *water-P* analyzed with ICP-MS has a stronger correlation with *AB-P*, *Morgan-P*, *Bray-1-P* and *Bray-2-P* ($r > 0.60$). Likewise, other studies

(Adesanwo et al., 2013; Kumaragamage et al., 2007; Maguire & Sims, 2002; Wuenscher et al., 2015) reported strong positive correlation between environmental P methods (water and $CaCl_2$) and agronomic methods. Additionally, a positive correlation between *water-P*, *Mehlich-3-P*, *Olsen-P*, and the dissolved reactive P in runoff collected from incubated soils treated with simulated rainfall was reported by another study (Kumaragamage et al., 2011). Furthermore, Wang et al. (2015) reported a correlation greater than 0.60 between *water-P* and agronomic P-*tests* (Olsen-P, Bray-1-P and Mehlich-3-P) (Wang et al., 2015), which supports the finding in this study. Thus, the relationship between environmental and agronomic P-*tests* evaluated in this study was affected by the methods of analysis, i.e., the species of P measured in the extract and the selection of P-*test.* For the tested Nfld acidic soils, the colorimetric-analysed *Mehlich-3-P* has a better capacity to reflect the environmentally relevant *water-P*; however the P saturation ratio or index has been alternatively proposed to overcome the weaker correlation of ICP-MS analysed *Mehlich-3-P* with *water-P*.

Moreover, as shown in Table 3.2, a strong, significant correlation was obtained between selected agronomic P-*tests* as analyzed with colorimetry ($r>0.84$) or ICP-MS ($r>0.64$). Specifically, a strong correlation was found between *Bray-1-P* and *Mehlich-3-P* analyzed with colorimetry ($r = 0.96$) or ICP-MS ($r = 0.84$) (Table 3.2 and Table 3.3). In agreement with these findings, other studies from North America reported a strong correlation between Bray-1-P and Mehlich-3-P (Culman et al., 2020; Hanlon & Johnson, 1984; Ketterings & Flock, 2005; Mallarino, 2003a; Tran et al., 1990) Also, another study found a strong correlation between *Bray-1-P* and *Olsen-P* for agricultural soils from the North Island of New Zealand (Sherrell, 1970), which is similar to this study ($r = 0.77$). Additionally, a

stronger correlation between Bray-2 and Mehlich-3 (r> 0.70) found in this study was supported by another study (Wang et al., 2004). Furthermore, in another study, good correlation was reported between Olsen and $CaCl_2$ (r = 0.60), and Olsen and citrate (r = 0.75) (DeLuca et al., 2015) while I found a weaker correlation between Olsen and $CaCl_2$ (r = 0.34) and relatively strong correlation between Olsen and citric acid (r = 0.84). The inconsistent correlation between agronomic P-*tests* could arise from extraction parameters like soil to solution ratio and shaking time and soil properties.

In particular, the citric acid extraction method extracted higher soil P regardless of the analysis method, which invites further investigation on which P species was primarily extracted. If the difference of soil P measured by ICP-MS (total P) and colorimetry (inorganic P) in citric acid extract reflect the actual organic P in the soil, which can be available to the plant upon microbial degradation (Dalal, 1977; Jørgensen et al., 2015; Margalef et al., 2017), consequently the P recommendation for different crops can be reconsidered for economic and environmental benefits.

Overall, in agreement with the literature, finding in this study indicates that the environmental and agronomic soil P can be predicted from agronomic *Mehlich-3-P* currently in use for Nfld Podzols.

3.4.6. Relationship Between Colorimetric and ICP Analyses Applied to Various P-*tests*

A strong correlation (r = 0.95) was found between *Mehlich-3-P* analyzed by colorimetry and ICP-MS, which is greater than the correlation (r = 0.84) reported in a study from State of Iowa (Mallarino, 2003b). The strong correlation obtained in both studies proves the

effectiveness of the Mehlich-3 method. Practically, Mehlich-3-ICP measures total P while Melich-3-Col measures available or soluble reactive P in the extract. Thus, different agronomic interpretation or indexes were suggested based on field calibration (Mallarino, 2003b).

Also, I found good correlation (r =0.80) between citric-P measured by colorimetry and ICP-MS, whereas another study reported a relatively strong correlation between citric-P analyzed with colorimetry and direct-current argon plasma emission spectrometry (Thompson, 1995). Any difference in correlations could be related to the analytical methods used for total P. Despite the differences, the citric acid method could potentially be used to estimate available organic P in the managed Podzols of Nfld rich in SOM.

Furthermore, a significant and strong correlation (r = 0.88) was found between *Bray-1-P* analyzed with colorimetry and ICP-MS, *Bray-1-P* analyzed with colorimetry and *Mehlich-3*-P analyzed with ICP-MS (r = 0.92), and *Bray-1-P* analyzed with ICP-MS and Mehlich-3-P analyzed with colorimetry (r = 0.85). In agreement with this finding, Ketterings and Flock (2005) and literature therein reported a strong correlation (r>0.85) between *Bray-1-P* and *Mehlich-3-P* analysed with colorimetry and ICP-AES representing various soil types (Ketterings & Flock, 2005). Moreover, Adesanwo et al. (2013) reported a strong correlation (r≥0.79) for P in manured and non-manured black Chernozem soils of Manitoba extracted by water, $CaCl_2$, Olsen, and Mehlich-3 analysed with colorimetry and ICP-AES) (Adesanwo et al., 2013). The lower correlation in this study could be explained by higher soil variability representing different depths, locations, management types, sensitivity of ICP-MS and wide range of measured soil P concentrations.

The *water-P* analyzed with colorimetric and ICP in this study has a weaker correlation (r = 0.36), while Adesanwo et al. (2013) found a strong correlation (r = 0.99) for the water-P measured with colorimetry and ICP-AES, the reason for the higher correlation in their later study could be attributed to manured soils used in the water extraction. Also, the type and properties of the soil might play a critical role in soil P extractability by water. In this study, I found a negligible correlation between *water-P* measured with colorimetric and SOM, whereas the relationship was improved for the *water-P* analyzed with ICP, which confirms that SOM has a direct influence on the quantity of *water-P* (Table 3.1).

Table 3.3. Pearson correlation between soil P extraction methods analysed with colorimetric and ICP-MS (separately). The bold values in the cells shows significant correlation ($p<0.05$).

		P-tests analysed by ICP-MS							
	P-tests	Water	Citric acid	AB	Morgan	Bray-1	Bray-2	Mehlich-1	Mehlich-3
P-tests analysed spectrophotometrically	Water	**0.36**	**0.43**	0.06	**0.23**	**0.51**	**0.52**	**0.29**	**0.59**
	Citric acid	**0.41**	**0.80**	0.14	**0.37**	**0.78**	**0.89**	**0.72**	**0.88**
	AB	0.13	**0.46**	**0.51**	-0.03	**0.36**	**0.38**	**0.29**	**0.37**
	Morgan	**0.29**	**0.37**	**0.33**	**0.67**	**0.26**	**0.43**	0.14	**0.43**
	Bray-1	**0.44**	**0.75**	0.09	**0.29**	**0.88**	**0.88**	**0.74**	**0.92**
	Bray-2	**0.50**	**0.72**	**0.34**	**0.53**	**0.78**	**0.92**	**0.67**	**0.82**
	Mehlich-1	**0.29**	**0.76**	0.03	0.13	**0.75**	**0.79**	**0.81**	**0.84**
	Mehlich-3	**0.50**	**0.75**	0.14	**0.38**	**0.85**	**0.90**	**0.71**	**0.95**

3.4.7. Multiple Linear Regression to Predict an Equivalent Agri-Environmental P from *Mehlich-3 P*

Linear regression is the most commonly used model to calibrate soil P measured in one *P-test* to against other *P-tests* (Ketterings & Flock, 2005; Kumaragamage et al., 2007; Wang et al., 2004). However, some studies recommend adding relevant soil properties like soil pH and texture to the equation (Wang et al., 2004). Thus, based on the soil P extractability comparisons, Pearson and multivariate correlation matrices of the extraction methods and

soil properties (Table 3.1, Table 3.2 and Table 3.3), polynomial equations were established between dependent (predictable soil P in selected methods) and independent (Mehlich-3 method) variables through incorporating surrogate variables using multiple regression analysis for both colorimetric and ICP-MS analyzed methods (Table 3.4). After several runs by adding or removing the surrogate variables to obtain better adjusted R^2 values and significant t-tests for the independent and surrogate variables, the surrogate variables or soil properties were included in the models to predict soil P in the methods of interest (Uyanık & Güler, 2013). Some methods, like AB and Morgan, were excluded because of their weak Pearson correlations with Mehlich-3. Also, in some cases, some soil variables were excluded as they have less impact on the predicted soil P variability (adjusted R^2) though they were significant in the model. As shown in Table 3.4, a strong adjusted R^2 (0.52-0.94) was obtained for calorimetry-obtained P predicted from Mehlich-3-P by controlling some soil properties significant in the model. A better determination coefficient ($R^2 = 0.69$) was obtained for the total water-P predicted from the total *Mehlich-3-P* analysed by ICP-MS by controlling for Ca, EC, and SOM properties of the soil (Table 3.4).

Also, adjusted R^2 values of 0.54, 0.75, 0.74, and 0.90 were obtained for citric acid, Bray-1, Bray-2, and Mehlich-1 methods, respectively (Table 3.4). Kumaragamage et al. (2007) reported a similar R^2 in predicting different soil P species from soil P analyzed by the Olsen extraction (Kumaragamage et al., 2007). Thus, different soil P species in the podzols of Nfld can be predicted from Mehlich-3 and selected soil properties, but this relationship should not be extrapolated to other similar regions (Gutiérrez Boem et al., 2011).

Table 3.4. Summary of multiple linear regression analysis parameters.

	Dependent	Parameters	Value	SE	t-Value	Prob>|t|	Adj. R-Square
Colorimetric	Water	Intercept	0.36806	0.10508	3.50264	0.00102	0.52
		Mehlich-3	0.01104	0.0015	7.3467	2.44E-09	
		EC	0.002	0.001	4.060	4.53E-04	
	Citric acid	Intercept	109.228	30.444	3.588	6.40E-04	0.90
		Mehlich-3	2.883	0.123	23.531	1.64E-33	
		Silt	-1.428	0.648	-2.204	0.03105	
	Olsen	Intercept	20.305	3.784	5.367	1.11E-06	0.63
		Mehlich-3	0.671	0.063	10.690	4.84E-16	
	Bray-1	Intercept	60.365	13.163	4.586	2.11E-05	0.94
		Mehlich-3	0.637	0.021	30.089	7.13E-40	
		pH	-9.170	2.086	-4.395	4.18E-05	
	Bray-2	Intercept	59.152	5.501	10.753	4.59E-16	0.75
		Mehlich-3	0.796	0.059	13.603	1.10E-20	
		Clay	-0.834	0.275	-3.030	0.00351	
	Mehlich-1	Intercept	40.492	14.104	2.871	5.54E-03	0.89
		Mehlich-3	0.416	0.024	17.223	1.02E-25	
		pH	-7.084	2.139	-3.311	0.00153	
		Clay	0.350	0.117	2.984	4.03E-03	
ICP-MS	Water	Intercept	-2.312	0.642	-3.602	8.46E-04	0.69
		Mehlich-3	0.036	0.006	6.110	3.02E-07	
		Ca	-0.011	0.004	-2.767	0.00844	
		EC	0.009	0.003	2.498	0.0166	
		SOM	0.245	0.068	3.605	8.37E-04	
	Citric	Intercept	148.464	21.523	6.898	2.46E-09	0.54
		Mehlich-3	2.869	0.321	8.925	5.91E-13	
	Bray-1	Intercept	192.090	49.230	3.902	2.29E-04	0.75
		Mehlich-3	0.957	0.076	12.662	3.31E-19	
		pH	-30.690	7.794	-3.938	2.03E-04	
	Bray-2	Intercept	19.473	9.304	2.093	0.04021	0.74
		Mehlich3	1.903	0.139	13.693	5.85E-21	
	Mehlich-1	Intercept	19.986	3.668	5.449	2.62E-06	0.90
		Mehlich-3	0.646	0.036	18.118	3.54E-21	
		Fe	-0.045	0.018	-2.573	0.01381	
		K	-0.043	0.015	-2.759	0.00863	
		EC	-0.052	0.014	-3.788	4.89E-04	

3.5. Conclusion

The soil P extractability was assessed and compared for different agri-environmental *P-tests* for Nfld Podzols with heterogenous characteristics, mainly management relevant or induced, were used to evaluate the soil P extraction methods' applicability and consistency in Nfld Podzols. The soil P extractability with Mehlich-3 was consistent with Bray-1 and Olsen agronomic P-*test* methods. On the other hand, Bray-2 and citric acid methods extracted 2-6-fold more soil P than Mehlich-3, which can be used to measure accumulated non-labile and organic P pools. The better relationship observed between water-extractable soil P with Mehlich-3 can be used to establish a critical limit for Nfld agricultural soils for environmental P management purposes. The selected soil properties have an inconsistent correlation with P-*tests*, regardless of the analysis techniques. However, a strong correlation was observed between some agri-environmental P-*tests,* and also multiple linear regression equations were developed by controlling relevant soil properties (adjusted R^2=0.52-0.94). The relationship between these methods or selected methods with crop yield or P uptake by plant must be developed for podzolic soils in Nfld.

3.6. References

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3.7. Supplemental Material

Description of soil P tests

The selection of a P-*test* is complex and region or soil specific. Thus, I applied the following extraction methods to measure the available and total P in the Podzols representing east, central, and west Nfld.

(a) **Water**: The water-extractable P is the most labile P pool and represents the instantaneous P supply to roots through mass flow effect. Deionized water was used to extract P at a 1:10 soil: water ratio (Carter & Gregorich, 2008; Wang et al., 2015).

(b) **Bray-1**: The Bray-1 extraction(Bray, R.H. ; Kurtz, 1945) uses an ammonium fluoride (0.03N) plus dilute hydrochloric acid (0.025N) solution. It extracts easily available acid-soluble P forms, which are thought to be a good indicator of plant-available P in soils dominated with aluminium (Al) and iron (Fe)(Jones, 2001). This method has been used to extract P in acidic to slightly neutral soil levels (pH<6.8) (Ketterings & Flock, 2005).

(c) **Bray-2**: The Bray-2 extraction similarly uses ammonium fluoride plus dilute hydrochloric acid extraction solution as for Bray-1. In the Bray-2, more concentrated hydrochloric acid is used, which can extract a non-labile P in slightly alkaline soil (Jones, 2001). The fluoride ions in the Bray-2 solution extract Al-bound P by forming Al-F complexes and prevent reprecipitation of P with colloids (Wuenscher et al., 2015). Both Bray-1 and Bray-2 are recommended to use in acidic soils (Tan, 2005). Before 2013, Bray-2 was used by the NL provincial soil

laboratory for nutrient recommendation purposes but they later changed to Mehlich-3 (Ziadi et al., 2013).

(d) **Mehlich-1**: The Mehlich-1 extraction solution involves hydrochloric acid and sulfuric acid. Mehlich-1 solutions can simultaneously extract P, potassium (K), calcium (Ca), magnesium (Mg), manganese (Mn), copper (Cu), and zinc (Zn) from acidic soils (Durackova, 1994).

(e) **Mehlich-3**: Mehlich-3 extraction was developed to cover a wide range of soil types (Carter & Gregorich, 2008). Mehlich-3 was modified from Mehlich-1 and Mehlich-2 to include copper, among other macro and micronutrients available in the soil, which can be determined with an inductively coupled plasma (ICP) method (Jones, 2001; Ketterings & Flock, 2005). Mehlich-3 extraction solution prepared from the combination of acetic acid, nitric acid, ammonium nitrate, ammonium fluoride, and EDTA (Mehlich, 1984; Wuenscher et al., 2015). Several countries currently use this method for agronomic and environmental P determination (Ketterings & Flock, 2005; Pellerin et al., 2006; Wuenscher et al., 2015). Mehlich-3 is the standard method currently practiced by several soil laboratories in North America, including the NL provincial soil laboratory (Pellerin et al., 2006).

(f) **Olsen**: This method uses a sodium bicarbonate solution to extract available P in soils with a pH range from neutral to alkaline by dissolving P bound to Ca and Fe (Olsen et al., 1954). It has also been used for acidic soil (Bair, 2012). This method tends to extract soil organic P (Tan, 2005).

(g) **Unbuffered 0.01M $CaCl_2$ solution**: Calcium chloride ($CaCl_2$) has been used as an alternative to water extraction. It extracts less available P compared to water due to the soil surface absorptive activity of calcium ions (Kuo, 1996).

(h) **Morgan**: This method uses an acetate-acetic acid solution buffered at pH 4.8 (Jones, 2001; Ketterings & Barney, 2010). Morgan's solution targets easily soluble and plant available P species in acid soils with less than 200 meq kg^{-1} cation exchange capacity (Jones, 2001). Morgan's soil test for P has been used for soil fertility guides and environmental risk assessments (Daly, 2005).

(i) **Ammonium bicarbonate diethylenetriaminepentaacetic acid (AB)**: This method uses a mixture of 0.005M diethylenetriaminepentaacetic acid and 1M ammonium bicarbonate solution buffered at pH 7.6 (Soltanpour, 1985). This method can extract labile P from calcium phosphate by precipitating calcium as calcium carbonate (Jones, 2001; Soltanpour, 1985). Also, this method is used to extract multiple elements and is considered to be as universal extractant (Soltanpour, 1985).

(j) **Citric acid (1%)**: A 1% citric acid solution used to extract available P in the soil. This method extracts P by solubilizing Al, Fe, calcium phosphates, and a portion of organic P in the soil. Also, a 1% solution of citric acids can extract multiple elements in the soil (Thompson, 1995).

Table S3.1. Summary of soil P extraction protocols

Methods	Extractants	Working Concentration	Soil: Solution (w/v)	Shaking time	Method of analysis
Deionized water	H_2O	NA	1:10	1 h	Colorimetry & ICP-MS
Bray-1	HCl NH4F	0.025N 0.03N	1:10	5 min	Colorimetry & ICP-MS
Bray-2	HCl NH4F	0.1N 0.03N	1:10	5 min	Colorimetry & ICP-MS
Olsen	$NaHCO_3$ NaOH polyacrylamide	0.5M NA 0.05%	1:20	30 min	Colorimetry
*Mehlich-1	H_2SO4 HCl	0.025N 0.05N	1:5	5 min	Colorimetry & ICP-MS
Mehlich-3	NH_4F EDTA NH_4NO_3 CH_3COOH HNO_3	0.015N 0.001M 0.25N 0.2N 0.013N	1:10	5 min	Colorimetry & ICP-MS
*Morgan	$NaC_2H_3O_2.3H_2O$ Glacial (CH_3COOH) DTPA	0.05N NA NA	1:5	5 min	Colorimetry & ICP-MS
AB§	DTPA NH_4HCO_3	0.005 M 1M	1:2†	15 min	Colorimetry & ICP-MS
$CaCl_2$	$CaCl_2.2H_2O$	0.01M	1:10	2 h	Colorimetry
Citric acid‡	$C_6H_8O_7$	1%	1:10	1 h	Colorimetry & ICP-MS

†LFH soil samples were 5 g in 20 mL; * LFH soil samples were 3g in 30 mL.
‡30 mL of 1% citric acid preheated to 70°C added to soil, the sample placed in a forced-draught oven at 70°C for 1 h and shaken vigorously by hand for 30 sec every 15 min (Thompson, 1995),
§Ammonium Bicarbonate DTPA (diethylenetriaminepentaacetic acid).

Table S3.2. *Descriptive statistics (sample size, n, mean and standard deviation, SD) of selected soil properties by location, management, and depth/horizon.*

	Locations	SJRDC, Eastern Nfld				Cormack, Western Nfld				CAFD, Central Nfld				
	Management type	Managed		Forested		Managed		Natural Buffer		Managed		Forested		
	Depth (cm)	0-20	20-40	LFH	B	0-10	10-20	0-10	10-20	Ap	E	LFH	E	B
Soil properties	n	23	23	3	3	8	8	4	4	5	3	4	4	4
pH	Mean	6.28	6.25	5.05	5.03	5.93	5.89	6.27	6.07	4.8	5.36	3.47	5.23	3.74
	SD	0.41	0.37	0.16	0.29	0.36	0.35	0.08	0.4	0.05	0.03	0.13	0.05	0.01
EC ($\mu S\ cm^{-1}$)	Mean	239.27	145.97	192.9	99.73	na	na	na	na	171.8	21.65	91	82.02	25
	SD	74.71	60.36	21.53	38.44	na	na	na	na	0.92	0.29	5.31	18.78	0.35
SOM (%)	Mean	12.57	9.31	47.23	12.97	7.30	6.44	8.35	4.81	3.9	0.74	21.5	4.23	3.24
	SD	2.61	2.05	0	0	3.10	3.26	5.94	1.60	0.6	0.07	1.43	1.05	0.05
Sand (%)	Mean	32.44	41.71	na	43.85	31.57	29.74	33.26	28.24	56.8	48.93	na	61.6	35.6
	SD	5.46	6.96	na	5.03	3.07	3.54	5.1	4.59	2.68	2.31	na	2.31	0
Clay (%)	Mean	17.98	15.63	na	17	31.06	35.05	29.5	32.08	8.36	6.96	na	6.96	9.46
	SD	2.25	1.91	na	0	4.61	1.33	6.72	5.86	1.67	1.73	na	0	0.58
Silt (%)	Mean	49.59	42.66	na	39.15	37.37	35.21	37.24	39.68	34.84	44.11	na	31.44	54.94
	SD	5.03	5.82	na	5.03	2.37	3.82	5.79	7.33	1.67	4.04	na	2.31	0.58
Al ($mg\ P\ kg^{-1}$)	Mean	1239.94	1747.64	1551.13	2131.2	1725.15	1722.75	1650.57	1480.03	2134.59	2110.36	1109.03	1927.17	1552.69
	SD	235.2	229.84	28.94	373.81	134.37	139.04	447.33	198.95	35.31	245.54	152.54	387.75	341.65
Fe ($mg\ P\ kg^{-1}$)	Mean	189.82	159.95	85.05	32.02	15.85	19.84	27.7	16.2	8.82	9.6	71.35	7.24	4.71
	SD	46.34	45.29	25.19	17.03	3.43	5.73	23.64	10.87	1.1	0.35	33.86	0.01	4.3
K ($mg\ P\ kg^{-1}$)	Mean	190.95	76.49	48.17	14.42	103.06	79.37	78.19	49.31	54.56	20.08	74.75	20.86	24.3
	SD	76.04	48.85	12.09	7.82	23.35	45.67	58.1	48.26	13.34	3.76	11.05	20.78	11.26
Ca ($mg\ P\ kg^{-1}$)	Mean	195.93	122.46	291.96	80.23	380.21	345.59	325.64	239.62	105.15	57.14	390.73	196.23	154.29
	SD	51.7	47.82	42.56	35.95	98.78	112.32	218.47	183.1	35.16	13.88	21.65	204.94	140.05

Note: Al, Fe, K, and Ca were extracted by Mehlich-3 and analyzed ICP-MS. Not analyzed (na).

Table S3.3. *Descriptive statistics of soil P (mg P kg^{-1}) extracted by 10* P-*tests and analysed by colorimetric methods and grouped by location, management, and depth/horizon (total sample =96).*

P-*test*	Locations	SJRDC, Eastern Nfld				Cormack, Western Nfld				CAFD, Central Nfld					Total
	Management	Managed		Forested		Managed		Natural		Managed		Forested			
	Depth (cm) /horizon	0-20	20-40	LFH	B	0-10	10-20	0-10	10-20	Ap	E	LFH	E	B	
	n*	23	23	3	3	8	8	4	4	5	3	4	4	4	96
Water (mg P kg^{-1})	Mean	0.79	13.25	2.12	0.31	1.48	1.34	1.27	0.67	0.2	0.1	bd	0.32	1.27	3.83[a]
	SD	0.47	9.45	2.44	0.17	0.58	0.68	1.07	0.33	0.08	0.03	bd	0.1	0.06	7.03
CaCl2	Mean	0.05	0.02	1.83	bdl	0.08	0.11	0.13	0	bdl	bdl	38.59	bdl	0.3	1.71[a]
	SD	0.16	0.1	2.31	bdl	0.21	0.3	0.26	0	bdl	bdl	21.77	bdl	0.35	8.66
Citric Acid	Mean	166.33	116.92	96.8	65.23	314.52	269.77	234.79	210.03	121.56	16.61	78.74	7.89	11.58	151.09[c]
	SD	108.32	80.93	44.68	36.84	86.53	116.12	123.91	121.68	47.29	3.28	15.78	3.28	3.99	118.18
Olsen	Mean	54.78	32.32	38.63	15.13	85.04	67.03	62.68	47.92	66.84	5.51	39.56	2.2	10.88	45.67[b]
	SD	30.95	25.05	19.55	13.88	24.71	24.45	30.35	32.55	14.51	0.18	13.37	0.36	1.79	32.06
AB	Mean	5.42	3.84	10.13	2.14	45.08	39.58	3.12	1.79	8.01	1.2	15.02	0.62	2.02	11.05[a,d]
	SD	3.22	2.85	2.81	1.01	47.23	41.67	1.96	0.79	1.3	0.03	3.33	0.15	0.23	22.47
Morgan	Mean	3.99	2.48	7.34	2.14	3.65	2.26	1.66	1.79	6.2	1.2	20.55	0.62	2.02	3.89[a]
	SD	2.51	2.07	5.83	1.01	1.09	1.21	1.96	0.79	3.46	0.03	9.72	0.15	0.23	4.81
Bray-1	Mean	30.19	15.04	39.99	10.42	65.59	54.83	58.02	39.09	38.39	10.93	48.26	2.12	11.66	31.42[b]
	SD	21.59	16.44	16.24	8.62	11.69	18.69	19.89	29.57	11.76	2.77	3.1	0.79	3.7	24.47
Bray-2	Mean	82.69	61.52	74.67	37.66	98.45	89.55	90.78	79.85	113.73	55.83	62.64	7.6	18.75	72.21[e]
	SD	32.77	33.29	6.23	22.23	13.55	19.16	19.37	21.03	14.06	12.27	7.07	3.5	5.55	34.48
Mehlich-1	Mean	17.59	13.47	27.76	9.19	57.34	46.37	32.83	31.34	44.75	16.4	49.66	0.99	4.92	25.07[d]
	SD	15.75	12.29	6.96	6.79	20.76	21.65	16.28	11.04	13.05	3.48	6.63	0.36	1.09	21.35
Mehlich-3	Mean	44.16	21.85	29.86	6.77	94.79	78.59	73.1	43.73	47.47	17.27	44.45	17.38	18.19	41.68[b,d]
	SD	32	21.91	9.11	5.97	25.15	33.7	44.83	45.84	12.14	2.86	8	19.81	11.98	34.66

* sample size for water (92), AB (88), Morgan (93), Mehlich-1 (94), Mehlich-3 (94). A similar letter in the column indicates no significant difference between the mean of the extraction methods at alpha 0.05.

Table S3.4. *Descriptive statistics of soil P (mg P kg^{-1}) extracted by 8* P-*tests and analyzed by ICP-MS (result grouped by location, management, and depth/horizon).* *(total sample =96).*

P-*test*	Locations	SJRDC, Eastern Nfld				Cormack, Western Nfld				CAFD, Central Nfld					Total
	Management	Managed		Forested		Managed		Natural		Managed		Forested			
	Depth (cm)/	0-20	20-40	LFH	B	0-10	10-20	0-10	10-20	Ap	E	LFH	E	B	
	n	23	23	3	3	8	8	4	4	5	3	4	4	4	96*
Water	Mean	2.66	0.77	12.60	2.32	1.60	0.99	2.18	1.13	0.15	BDL	89.41	0.13	1.84	5.68[a]
	SD	2.24	0.62	8.04	1.88	2.23	0.91	2.42	1.09	0.12	BDL	46.52	0.08	0.95	20.04
Citric Acid	Mean	283.52	217.31	137.44	147.67	433.16	438.30	358.72	307.54	137.14	296.79	373.26	254.13	440.48	290.19[b]
	SD	148.30	112.21	68.21	52.37	211.01	151.82	70.63	112.18	73.94	27.34	165.32	3.42	27.24	154.32
AB	Mean	15.87	10.83	20.00	19.08	6.07	4.08	6.15	4.80	18.39	2.22	29.81	4.64	12.60	12.53[a]
	SD	4.90	3.53	0.88	6.35	0.89	1.07	2.27	2.40	3.83	0.10	2.69	1.26	0.14	7.12
Morgan	Mean	10.02	6.42	12.48	10.87	6.48	5.28	5.71	4.09	7.00	8.75	29.86	1.57	3.39	8.17[a]
	SD	3.08	2.38	0.75	4.26	1.24	1.57	2.25	2.60	2.49	0.00	9.06	0.23	0.42	5.95
Bray-1	Mean	53.78	28.67	79.21	30.56	95.66	76.82	80.02	48.95	67.81	15.86	83.23	5.14	18.81	51.42[c]
	SD	57.00	35.02	20.92	14.36	33.34	38.09	39.70	42.68	19.84	3.82	9.93	1.65	5.46	44.91
Bray-2	Mean	125.03	80.95	96.30	43.14	195.16	157.73	142.45	109.04	254.47	51.50	78.69	8.04	19.84	112.90[d]
	SD	106.52	69.22	9.73	23.52	61.73	76.75	65.28	55.32	54.14	10.21	6.60	4.58	5.13	89.99
Mehlich-1	Mean	25.74	19.22	61.63	17.32	46.96	56.34	40.40	51.04	56.94	20.40	69.19	3.81	9.36	32.29[a,c]
	SD	19.27	13.61	3.82	8.33	19.16	21.82	18.31	29.38	15.57	3.57	18.33	0.61	1.53	23.81
Mehlich-3	Mean	53.74	27.27	48.17	14.42	103.06	79.37	78.19	49.31	54.56	20.08	74.75	20.86	24.30	49.47[c]
	SD	34.01	21.79	12.09	7.82	23.35	45.67	58.10	48.26	13.34	3.76	11.05	20.78	11.26	37.13

*sample size for water (92), AB (88), Morgan (93), Mehlich-1 (94), Mehlich-3 (94). A similar letter in the column indicates no significant difference between the mean of the extraction methods at alpha 0.05. Below detection limit (BDL).

Chapter 4. PHOSPHORUS ADSORPTION IN FORESTED AND MANAGED PODZOLIC SOILS

4.1. Abstract

Despite the agricultural expansion into the boreal ecoregion of Canada, little is known about the phosphorus (P) adsorption capacity in the soil profiles of natural and managed Podzols. This information is critical for informing management decisions for P use efficiency and mitigating related environmental risks. Thus, this study aimed to evaluate P adsorption of podzolic horizons in natural and managed soil using nonlinear Langmuir and Freundlich adsorption models. A batch adsorption experiment was conducted using soils collected from distinct horizons of forested and managed fields in eastern and central Newfoundland, Canada. Nonlinear Langmuir and Freundlich fitted models had correlation coefficients (r) greater than 0.99 regardless of soil horizons, locations, and management history. The organic LFH, a surface horizon common for forested podzols, and a long-term *managed* Ap horizon had the highest P retention capacities when compared to either newly converted soils or soils used as tree nursery following conversion from natural forest. The maximum P adsorption capacity was positively correlated with the water extracted labile P, Mehlich-3 extracted Ca, and clay contents while negatively correlated with the horizons' median depths. Results suggest that following conversion from forest to agricultural use, long-term management that includes tillage, lime and fertiliser application creates an Ap horizon with strong adsorption capacity, but which could still serve as both sink and source

of P. The newly converted soils and the deeper soil horizons, for both natural and converted lands, do act mainly as P sinks.

Keywords: Phosphorus, adsorption isotherm, adsorption capacity, Podzols, Newfoundland

4.2. Introduction

The biogeochemistry of soil phosphorus (P) is complex and governed by numerous factors, including soil type, soil management and use, vegetation type, and local environmental factors. Understanding the capacity of the soil to adsorb P is critical in determining the best nutrient management plan for enhancing the agronomic value of P fertilisers and also mitigating related environmental risks (Olsen and Watanabe, 1957; Sims and Pierzynski, 2005; Ulrich and Schnug, 2013). The increased utilisation of P fertiliser following the Green Revolution (Cordell, Drangert, & White, 2009) and expansion of the dairy industry (Barnett, 1994; Kinley et al., 2007; Achat et al., 2014; Liu et al., 2018; Cordeiro et al., 2019) resulted in P applications above the amounts needed by the crops.

Usually, a small proportion of the P added to the soil in chemical and organic fertilisers is expected to remain soluble in the soil solution and be accessible to plant roots (Jianbo et al., 2011). However, depending on the soil properties, a significant amount of P can be fixed by sesquioxides of aluminium (Al) and iron (Fe), clay minerals (Eriksson et al., 2016; Luo et al., 2017; Roy et al., 2017), soil organic compounds (Read and Campbell, 1981; Debicka et al., 2015; Eriksson et al., 2016), and poorly crystalline Al and Fe oxyhydroxides (Ayenew et al., 2018). Most P fertiliser thus ends up in chemically fixed forms and stored

in the soil (Roy et al., 2017). This soil residual P or accumulated legacy P (Luo et al., 2017; Roy et al., 2017) has a high probability entering adjacent catchments (Haygarth et al., 2014) posing an increased risk of freshwater pollution through eutrophication (Bailey et al., 2016; Bunting et al., 2016; Malley & Watts, 2016; Schindler et al., 2016; Ulén et al., 2007; Wang et al., 2016; Warrinnier et al., 2019).

Cold humid region, low fertility soils are generally sandy and characterized by high acidity, high organic matter, Fe, Al, and low water-holding capacity (Simard et al., 1988; Sanborn et al., 2011; IUSS Working Group WRB, 2015); they are classified as Podzols in the Canadian (Canadian Agricultural Services Coordinating Committee, 1998; Sanborn et al., 2011) and Food and Agriculture Organization (FAO) soil classification systems or as Spodosols in the United States Department of Agriculture (USDA) soil classification system. The eluviated (E) horizon of Podzols, usually underlying an organically rich LFH horizon, has low organic matter horizon, is sandy and acidic; the deeper illuvial B horizon, has elevated levels of clay, accumulated organic matter and metal oxides (Sanborn et al., 2011; Grand and Lavkulich, 2013; IUSS Working Group WRB, 2015).

Understanding P sorption characteristics of specific soils is essential for ensuring agronomic and environmental sustainability of land uses (Wang et al., 2016; Roy et al., 2017; Sharma et al., 2017; Yan et al., 2017; Nobile et al., 2018). P adsorption in Podzols, particularly by each of their soil horizons, has not yet been carefully investigated (Väänänen et al., 2008; Villapando & Graetz, 2001). These questions become more pressing as the expansion of agriculture into the boreal region accelerates. The changes in physical and chemical properties of the converted soil, their temporal stability and their impact on nutrient dynamics have not yet been consistently investigated.

Aluminium and Al-organic complexes are responsible for P adsorption in the spodic Bh profile of selected Florida Podzols (Villapando & Graetz, 2001). On the other hand, a Finnish study reported that Fe was the dominant mineral species responsible for P retention in the O, E, B1, and B2 horizons, although the studied Podzol was rich in Al. Calcium P fixation mechanism dominated in C horizons of a Finnish boreal Podzol, a reflection of the original parent material conditions (Väänänen et al., 2008). The same study confirmed that P mobilized from the E horizon was retained and fixed in the B1 and B2 horizons, which hindered P leaching to groundwater (Väänänen et al., 2008). Another study, also from Finland, reported P sorption characteristics of three Inceptisols, and one Podzol soil horizon, which concluded that fertiliser had an impact on P sorption by the Ap horizon, as inferred from legacy P effects. In contrast, the illuvial B horizon had a higher P sorption capacity linked to higher Al and Fe content (Peltovuori, 2007).

Thus, the transport and accumulation of P in the C horizon depends on the amount and type of P applied as fertiliser or manure, amount and type of fixed and exchangeable cations in soil, and the soil horizonation as a function of the management type and intensity. Plant roots can also provide a small amount of P to the subsoil from the firmly fixed Ca-P species (Read and Campbell, 1981).

To my knowledge, the P adsorption-desorption in the Newfoundland and Labrador (NL) soils has not been yet investigated. Nevertheless, NL has policies and subsidizes the expansion of agricultural lands through the conversion of boreal forests (Government of Newfoundland and Labrador, 2017). The working hypothesis for this study is that the P adsorption capacity of podzolic horizons will be different in forested versus managed soils, an effect of land-use conversion and subsequent management. During deforestation for

conversion to agricultural use, the O or LFH horizons are removed, and the E and B horizons mixed during land preparation (tillage) (Lindroos et al., 2016; Väänänen et al., 2008). Consequently, for new conversions, the organic content of the affected Podzol is diminished, and the probability of further organic-P complexation decreased. On the other hand, P may be firmly fixed by soil minerals and thus made unavailable, rendering the soil mainly a P sink. The effects on P sorption of subsequent soil management involving tillage, liming and fertilisation, under various cropping systems must be understood to allow for the development of sustainable P management strategies for such soil conversions.

The goals of this study are to: (1) investigate the P sorption behaviour of *managed* and *forested* Podzols horizons; (2) assess the putative maximum P adsorption capacity of the same soils; and (3) predict P adsorption capacity of *managed* and *forested* boreal Podzols on the island of Newfoundland (Nfld).

4.3. Materials and Methods

4.3.1. Site Description

Soil samples were obtained from two locations: (1) Agriculture and Agri-food Canada (AAFC) St. John's Research and Development Centre (SJRDC), NL (47.56° N, 52.71° W), at an elevation ~114 m above sea level (asl) with an annual mean rainfall of 1534 mm and an annual mean temperature of 5 °C; and (2) the Centre for Agriculture and Forestry Development (CAFD), Wooddale, NL (49.03° N, 55.55° W), at an asl of ~46 m with an annual mean rainfall of 1108 mm and an annual mean temperature of 4.4 °C (Government of Canada, 2019).

The two locations have distinct management histories. The relatively young *forested* SJRDC soil lacks an E horizon, a residual effect of the relatively recent disturbance (about 25 years ago), which did not allow yet for significant re-podsolization after replantation with black spruce (*Picea mariana*). The *forested* CAFD soil has well-developed podzolic soil horizons (LFH, E, B, BC, and C). The SJRDC *managed* field has been in agriculture for about 150 to 160 years. Historically, most SJRDC fields are managed under a mix of timothy (*Phleum pratense*), red clover (Trifolium pratense) and alsike clover (*Trifolium hybridum*) in rotation with crop research experiments. The fields receive variable amounts of mineral fertiliser or manure and are regularly limed (Woodrow et al., 1996, unpublished report).

The CAFD *managed* field was under forest management for 30 years, used as a tree nursery with a history of fertiliser application, in support of large-scale reforestation following the destruction of about half a million hectares of forest during a 1961 fire (Government of

Newfoundland and Labrador, 2019). Just before sampling, in August 2017, the *forested* CAFD field was being converted to agricultural use.

SJRDC soil is an Orthic Humo Ferric Podzol (Heringa, 1981) developed on a glacial till whereas the CAFD soil is a Ferro-Humic Podzols developed on glaciofluvial deposits (Sanborn et al., 2011).

4.3.2. Soil Sampling

Soils were sampled between August and November 2017. About 1 kg of soil was collected from the identifiable horizons after digging 1.5 m deep and 1.0 m wide pits using a backhoe. The LFH, B, BC, and Ap, B, and C soil horizons were collected from the *forested* and *managed* SJRDC fields, respectively. The *managed* SJRDC soil does not have a visible E horizon likely an effect of the long-term, continuous agricultural management following the initial forest converted to agricultural use in the 1860s. At SJRDC, five locations were sampled in the *managed* fields and three locations in the adjacent *forested* area (Table 4.1). The LFH, E, B, BC, and Ap, E, and C soil horizons were collected from the *forested* and *managed* CAFD fields, respectively. The *managed* CAFD field lacked a distinct B horizon as the shallow original B horizon was disturbed and mixed during conversion to merge into a developing Ap horizon eventually. Soil samples along the profile depth were collected from two *forested* locations and three *managed* locations (Table 4.1). Soil samples collected from similar horizons of the same location and management were bulked together to obtain one representative sample. These by-horizon samples (n = 13) were characterized and used for obtaining P sorption isotherms.

Samples were stored at -10 °C until processed. Before analyses, samples were thawed at 4 °C for 72 h, air-dried for 3 to 5 d in a temperature-controlled room (~35 °C with air movement), and passed through a 2 mm size sieve.

Soils were analyzed for (1) soil organic matter (SOM) based on loss-on-ignition method at 430 °C, (2) total carbon (TC) and total nitrogen (TN) content using a CN928 LECO CNS analyser (LECO Corporation, St. Joseph, USA), (3) pH and electrical conductivity (EC) measured in 1:2 soil to double distilled water (DDW) ratio, and 1:5 soil to DDW ratio for soils with high organic matter content, (4) particle size distribution determined with hydrometer method (Carter & Gregorich, 2008), (5) mineralogical analysis with a Rigaku Ultima-IV Powder X-Ray Diffractometer (XRD) (Rigaku Corporation, Tokyo, Japan) at 2Theta/theta, 40kV and 44mA, (6) the available P in the soils extracted with Mehlich-3 in a 1:10 soil to solution ratio (Carter & Gregorich, 2008). The Mehlich 3 extract analyzed for micro and macronutrient using a Prodigy High Dispersion ICP-OES (Teledyne Leeman Labs, Manson, USA).

Table 4.1. Sampled soil horizons.

Management & Location	Horizon	Descriptions
Forested- SJRDC, Eastern Nfld	LFH	-Mixture of undecomposed and decomposed plant materials; minimal decomposed organic matter ~2 cm thick
	B	~16-20 cm thick
	BC	~12-18 cm thick
		-Transition profile between B and C horizons
Managed- SJRDC, Eastern Nfld	Ap	~23-27 cm thick
	B	-Mixture of BC found between B and C horizons, ~30-33cm thick
	C	~30 cm thick
Forested- CAFD, Central Nfld	LFH	~10-12 cm thick, mixture of undecomposed and decomposed plant materials
	E	~3-5 cm thick
	B	~15 cm thick
	BC	~10 cm thick
		-Transition profile between B and C horizons
Managed- CAFD, Central Nfld	Ap	~15-20 cm thick
	E	~10-15 cm thick
	C	~80-85 cm thick

4.3.3. Adsorption Experiment

Adsorption isotherms for 13 by-horizon samples were obtained with data from batch adsorption tests (Zhang et al., 2009). Tests were carried out using 0, 5, 25, 50, 100, 150, 250, 500, 750, and 1000 mg P L^{-1} in 0.01 M KCl electrolyte solution. A 2 ± 0.01g aliquot of air-dried soil was added to a 125 mL Erlenmeyer flask and saturated with 20 mL of the respective 0.01M KCl solution. Adsorption was assessed for a total contact time of 24 h: the mixture was agitated for 1 h on an end-to-end shaker (180 rpm) followed by equilibration at room temperature (~20 °C) for 22 h and eventually re-agitated for another 1 h (Väänänen et al., 2008). The soil-solution was filtered through a 0.45 µm filter paper (Jalali and Jalali, 2016). The equilibrium P in the filtrate was quantified using the ascorbic

acid method (Watanabe & Olsen, 1965). All experiments were conducted in triplicate. The results were corrected for oven-dry soil mass.

The P adsorption protocol was adopted from previous studies, with modifications for the electrolyte solution, shaking and contact time (Olsen and Watanabe, 1957; Bache and Williams, 1971; Ige et al., 2005; do Carmo Horta and Torrent, 2007; Jalali and Jalali, 2016). Microbial inhibitors like toluene or chloroform were not used as they favour lysis of microbial cells and increase dissolved P (Sims & Hodges, 2000). Adsorbed phosphate at equilibrium was calculated using the Equation (4.1):

$$q_e = \frac{(C_i - (C_e - C_o) \times V}{m} \quad \text{Equation (4.2)}$$

Where: q_e (mg P g^{-1} of soil) is the amount of phosphate adsorbed at equilibrium; C_i, C_e, and C_o are the initial, equilibrium, and labile P concentrations in mg P L^{-1}, respectively; V is the volume of the solution in litres (L) and m is the oven-dry soil mass in g (Chen, 2015).

4.3.4. Non-linear Langmuir and Freundlich Models

The non-linearized models of Langmuir and Freundlich (Chen, 2015; Subramanyam & Das, 2014) were used to fit the experimental data. The model parameters were estimated using the Origin program (Origin(Pro), Version 2019b. OriginLab Corporation, Northampton, MA, USA). The maximum P adsorption capacity of each soil horizon was determined from the Langmuir model (Chen, 2015; Subramanyam & Das, 2014). Despite theoretical limitations, the empirical models of the Langmuir and Freundlich models were widely applied in describing soil P adsorption isotherm data (Goldberg, 2005; Mead, 1981). The Langmuir model assumes an equivalent and limited monolayer (Kruse et al., 2015;

Villapando & Graetz, 2001) of adsorption sites on the soil, while Freundlich covers the heterogeneity of adsorption sites and also considers reversible adsorption behaviour of the soil even though it does not obey Henry's law to attain adsorption maxima (Goldberg, 2005). The Langmuir model is the most widely used for assessing P adsorption by soils for obtaining maximum adsorption capacity and P binding strength (Villapando & Graetz, 2001). The nonlinear Langmuir and Freundlich isotherm models are presented in Equations (4.2) and (4.3) (Chen, 2015; Subramanyam & Das, 2014).

$$q_e = q_{max} K_L \frac{(C_e - C_o)}{1 + K_L C_e} \quad \text{Equation (4.2)}$$

$$q_e = K_F (C_e - C_o)^{1/n} \quad \textit{Equation (4.3)}$$

Where C_e is the final concentration of P in the solution at equilibrium and C_o is the labile P in mg P L^{-1}; q_e is the corresponding soil P adsorption capacity at equilibrium plus native P in the soil (mg P g^{-1} of soil); q_{max} is the maximum P adsorption capacity on the soil monolayer (mg of P g^{-1} of soil), and K_L is adsorption/desorption of P at equilibrium or net enthalpy of adsorption (L mg^{-1}); K_F (mg g^{-1}) and n (L mg^{-1}) measures the capacity and intensity of adsorption, respectively.

The empirical constants, *i.e.*, q_{max}, K_L, K_F, and n are determined by fitting the data into nonlinear Langmuir and Freundlich models. In this study, the empirical constants were determined using OriginPro 2019b through a nonlinear least square regression curve fit using an orthogonal distance regression iteration algorithm at the lowest least of squared errors (Mead, 1981).

4.3.5. Statistics

Standard and explanatory statistical analyses were conducted using OriginPro 2019b and Past3 (Hammer et al., 2001) programs. Simple Pearson correlations and correlation matrix principal component analyses (PCA) were performed to identify the relation between adsorption parameters and soil properties. The components were selected based on the three criteria, *i.e.*, eigenvalues greater than 1, cumulative percent contribution (at least 70%), and individual component percent contribution (at least 5%) (Jalali & Jalali, 2016). The variables were only explained by the loading they contribute to each component. A one-way ANOVA with a post hoc Tukey's test was applied to compare the adsorption parameters across soil horizons. Stepwise multiple regressions were employed to assess the utility of soil variables to predict P adsorption parameters. The putative relationships between soil properties and P adsorption parameters were estimated with multivariate analysis (See Supplementary Material).

4.4. Results and Discussion

4.4.1. Characteristics of the Studied Soils

Soil parameters presented and discussed here are summarized in Table S4.1, Supplementary Material. At SJRDC, the *managed* Ap, *forested* B and B/C horizons were classified as loams, whereas the *managed* B and C horizons were classified as sandy loams. At CAFD, *forested* and *managed* soil horizons were classified as sandy loam except for the E horizon, which was classified as a silty loam (Table S4.1). The XRD analysis showed that *quartz* is the most abundant mineral phase, followed by *albite, clinochlore*, and *muscovite; the* mineralogy was similar across the tested sites (Table S4.2).

At SJRDC, *forested* soil horizons had a pH of around 5.0, while all *managed* horizons had a pH of about 6.0, a result of long-term lime applications for suppressing Al toxicity. On the other hand, the pH in the *forested* CAFD soil increased from 3.4 in LFH to 5.2 and 5.4 in B and B/C horizons, respectively. A similar decrease in acidity with depth was measured for the *managed* CAFD horizons from 4.8 for Ap to 5.7 for C. These trends are in line with reported gradients in Podzols (Abedin, 2018; Heringa, 1981; Väänänen et al., 2008). The decrease in soil acidity with depth is related to the vertical mobility, *i.e.* chilluviation, of basic cations in Podzols (Grand & Lavkulich, 2013).

The *forested* SJRDC soils had large organic matter contents at the surface but decreased rapidly with depth. While the *managed* top horizon at SJRDC had a large SOM of about 11%, the SOM in the topsoil of the newly converted CAFD *managed* soils was 3.6% decreasing very rapidly with depth to <0.5 % in the C horizon. The SJRDC reflects a long history of management for organic matter, including manuring, while the CAFD is direct

evidence of the low SOM in newly converted soils from which the surface LHF layers have been removed, as also observed for land-use conversions in Labrador (Abedin, 2018). As expected, the TN values followed the SOM trends.

EC, CEC and cations concentration decreased with depth, while Al increased with depth, typical trends for podzolic soils (Schnitzer & Desjardins, 1969).

The Mehlich-3 method was able to extract more labile P and moderately non-labile P from the top LFH, Ap. The illuvial B horizons had lower Mehlich3-P concentrations, an indication of the P being firmly fixed by Al. An increase in the C horizon Mehlich3-P might be due to the dissociation of apatite (Tran et al., 1990) or, less likely given the Al-rich overlaying B horizon, indicative of downward P mobility. The Podzols in this study have a P saturation index (P/Al+Fe) lower than agricultural soils of Ontario or Maritime provinces of Canada (Benjannet, Khiari, et al., 2018; Benjannet, Nyiraneza, et al., 2018; Wang, Zhang, et al., 2015).

4.4.2. Phosphorus Adsorption

Experimental data fits well with both nonlinear Langmuir and Freundlich adsorption isotherms (R^2>0.99 goodness of fit). At SJRDC, the maximum P adsorption capacity (q_{max}) decreased notably with depth (

Table 4.2), with both *forested* LHF and *managed*-Ap having comparatively large adsorption capacities. The newly converted *managed* CAFD had uniform q_{max} with a depth similar to the mineral horizons of the *forested* CAFD soils. Compared to alkaline soils, acid soils have a high q_{max} due to a larger surface area and strong bonding energies (Olsen and Watanabe,

1957). The distinct q_{max} of the LFH at the two forested locations was surprising; the literature also has contradictory opinions on the role of SOM (47.2% for *forested* SJRDC; Table S4.1) (Väänänen et al., 2007; Yang et al., 2019) especially in the presence of Al and Fe (Table S4.1). In the mineral horizons of Podzols, however, the retention of P is dominated by Al and Fe (Väänänen et al., 2008). Depending on soil types and environmental factors (Debicka et al., 2015; Yang et al., 2019) four mechanisms were proposed for the interactions between P and SOM (Hunt et al., 2007): (a) formation of cation bridge to adsorb P, (b) phosphate ion a stronger competitor for adsorption sites than organic acids, (c) metal-organic complexation reduces P adsorption and (d) repulsion of phosphate ions by organic acids on the surface of metals. The first two mechanisms could explain the higher P adsorption by *forested* LHF and *managed* Ap horizons. The results confirmed both SOM and Al as positively correlated with q_{max}, but with Al and Fe dominant (Väänänen et al., 2007). A combination of high SOM in forested B-horizon and higher Al in B/C horizon might explain the apparently similar q_{max} values (Table 4.2). Organically bound Al ($CuCl_2$ extractable Al) has been previously reported to be responsible for 60% of P retention, of which most (about 70%) is non-labile P (Villapando & Graetz, 2001).

For the established agricultural field (*managed*-SJRDC), the Ap horizon had a significantly higher q_{max} (8.23 mg g^{-1}) than the underlying horizons (3.12 mg g^{-1} and 2.77 mg g^{-1} for the B and C horizons respectively). Moreover, the higher SOM B horizon had similar q_{max} with the low SOM C horizon. The C horizons may have higher total basic cations (Grand & Lavkulich, 2013) responsible for P retention; e.g., its Mn concentration was twice the content in the *managed* B horizon. Both *forested* horizons and *managed* horizons have statistically similar Langmuir adsorption/desorption rates (Table 4.2). The *forested* E, B,

BC, and *managed* Ap horizons with high clay contents and higher content of Al and Fe in the clay have higher q_{max} (Table 4.2).

The higher q_{max} for the newly converted soils (*managed* CAFD), relatively uniform across horizons, suggest that upon forest conversion to agriculture, these mineral horizons act as P sinks (Table 4.2), despite the smaller differences in measured P (Table S4.1). On the other hand, the high q_{max} in the older *managed* Ap (SJRDC) indicates that converted Podzols can eventually store large amounts of P in the root zone (Bauke et al., 2018). However, this might eventually increase the potential risks for the transfer of P to water bodies via erosion (Kleinman et al., 2015).

The results for the Nfld soils tested here show a higher q_{max} than for southern Finland *forested* Podzol horizons (Väänänen et al., 2008), about 4-11-fold higher than for Quebec Gleysols, 2-7-fold adsorption than Quebec podzolic soils (Laverdiere & Karam, 1984), 20-fold higher than Ontario soils in livestock production areas (Wang et al., 2015) and 40-fold higher than for the fertile Saskatchewan Mollisols (Rennie & McKercher, 1959). Also, tested Nfld Podzols P saturation index (P/Al+Fe) was about 15-40-fold higher than for Charlottetown sandy loam soil, a strongly acidic Orthic Humo-Ferric Podzol (Cade-Menun et al., 2010). These results confirm the strong sink capacity of Nfld Podzols.

Technical considerations regarding the experimental setup can be found in the Supplementary Material.

Table 4.2. A one-way ANOVA for phosphorus adsorption parameters for forested and managed soils.

Location & Management	Soil Horizon	q_{max}	K_L	K_F	n
		mg g^{-1}	----------L mg^{-1}----------		
SJRDC *Forested*	LFH	7.47(0.26)[a*]	0.052(0.009)	2.53(0.51)	3.58(0.38)
	B	5.08(0.11)[b]	0.025(0.002)	0.49(0.08)	3.39(0.10)
	BC	5.35(0.34)[b]	0.023(0.003)	0.22(0.02)	2.59(0.15)
SJRDC *Managed*	Ap	8.23(0.86)[a, c]	0.011(0.002)	0.14(0.03)	2.03(0.17)
	B	3.12(0.19)[d]	0.047(0.013)	0.23(0.06)	4.15(0.27)
	C	2.77(0.20)7[d]	0.012(<0.001)	0.02(<0.001)	2.77(0.09)
CAFD *Forested*	LFH	3.13(0.21)[a]	0.004(<0.001)	0.01(<0.001)	1.80(0.02)
	E	5.64(0.10)[b]	0.006(<0.001)	0.04(<0.001)	1.95(0.02)
	B	6.49(0.16)[c]	0.013(<0.001)	0.22(0.01)	2.60(0.04)
	BC	5.06(0.14)[b]	0.009(<0.001)	0.06(0.01)	2.34(0.03)
CAFD *Managed*	A	6.23(0.17)[b, c]	0.009(<0.001)	0.08(<0.001)	2.19(0.02)
	E	5.72(0.20)[b]	0.007(<0.001)	0.05(<0.001)	2.07(0.03)
	C	5.59(0.11)[b]	0.006(<0.001)	0.04(<0.001)	1.93(0.01)

*Same letters within a column, separately by location, imply statistical similarity (α = 0.05). Standard errors (n=3) in parentheses.

4.4.3. Correlation Between Phosphorus Adsorption Parameters and Soil Parameters

Both models described well the experimental observations (see the correlation in Table 4.3), also as previously reported (Mead, 1981). Though, the Freundlich equation does not provide q_{max}, the good relationship between the parameters of the two models confirmed both to be useful in determining P dynamics in Podzols.

Most CAFD soil horizons were not P saturated and had higher q_{max} (Table 4.2). This could be linked to a significant relationship of the Freundlich adsorption intensity (n) with the Al content (Fitter & Sutton, 1975) (Table 4.3).

A non-significant correlation was observed between q_{max} and Langmuir binding energy (K_L), whereas a moderate correlation with the Freundlich adsorption rate (K_F) was detected

(Table 4.3) suggesting a multilayer surface be responsible for the P adsorption (Börling et al., 2001). A significant relationship between the Freundlich adsorption constant (K_F) and n (Table 4.3) further demonstrated Freundlich adsorption to explain the P adsorption in Podzols (Peltovuori, 2007) despite the inability of providing a q_{max}.

In the tested soils, and likely other Podzols in Nfld, multiple compounds, Al and Fe hydr (oxides), organic acids, and metal-organic acid chelates, are likely responsible for P retention as described by the Freundlich model and the multivariate analysis (Table 4.4).

Table 4.3. Correlation between Langmuir and Freundlich P adsorption parameters and soil variables for forested and managed soil horizons (n=13).

Variables	Langmuir		Freundlich	
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	K_F (L mg^{-1})	n (L mg^{-1})
H_2O-srP (mg kg^{-1})	0.70**	0.84**	0.91**	0.46**
CA-srP (mg kg^{-1})	0.21	0.65**	0.61**	0.55**
M3-srP (mg kg^{-1})	0.14	-0.05	0.07	-0.30
M3-Ca (mg kg^{-1})	0.36*	0.38*	0.44**	0.17
M3-K (mg kg^{-1})	0.05	0.25	0.54**	-0.05
M3-P (mg kg^{-1})	-0.03	-0.13	0.16	-0.32*
M3-Fe (mg kg^{-1})	0.19	0.30	0.59**	0.01
M3-Al (mg kg^{-1})	-0.05	0.21	-0.11	0.45**
Median depth (cm)	-0.44**	-0.16	-0.36*	0.04
Clay (%)	0.39*	0.19	0.60**	0.16
Silt (%)	0.12	0.08	0.23	0.04
Sand (%)	-0.24	-0.13	-0.40**	-0.09
SOM (%)	0.24	0.56**	0.84**	0.25
TC (%)	0.04	0.37*	0.62**	0.09
TN (%)	0.31	0.60**	0.82**	0.32*
pH	0.12	0.29	0.06	0.40**
EC (µS cm^{-1})	0.29	0.35*	0.58**	0.10
qmax (mg g^{-1})		0.00	0.35*	-0.28
K_L (L mg^{-1})			0.73**	0.83**
K_F (L mg^{-1})				0.41**

*Significant at < 0.05 probability level.
**Significant at < 0.01 probability level.

4.4.4. Extrapolation of P Adsorption Using Soil Properties

The soil variables significantly correlated with adsorption parameters were used in a predictive exercise using a multivariate analysis of variance (MANOVA) in a stepwise regression approach.

The combination of horizon depth, clay content and SOM explained 36% of q_{max} variability by horizons; 20% of the variability was associated with the inverse of the median depth (Table 4.4). The combination of Mehlich-3 Al and Fe, SOM and pH explained 52% of the variability in K_L, of which 31% was described by the SOM alone (Table 4.4). Börling et al. (2001) reported that oxalate extractable Al and Fe were responsible for P adsorption in 35-40 years old agricultural soils.

Furthermore, SOM and Mehlich-3 Fe explained 71% and respectively, 35% of the variability in K_F (Table 4.4). On the other hand, the combination of Mehlich-3-total P (TP) and Al, SOM, and pH explained ≈50% of the variability in *n;* ≈20% of the variability was described by Mehlich-3 Al alone (Table 4.4). This could be related to the higher loading of the two variables in the PC2 and PC3 (Table S4.3). I may conclude that high P adsorption in the tested *forested* and *managed* Podzol horizons are mainly influenced by the combined effect of SOM, Al, and Fe.

Table 4.4. Stepwise multivariate regression results for the relationships between P sorption parameters and selected soil variables. Only significant variables are presented.

Dependent Variable[€]	*Independent Variable*	*Coefficient*	*Standard Error*	*Partial R^2*
q_{max}	Constant	2.31×10^{1}**	2.59	-
	Median depth	-7.74×10^{-2}**	9.73×10^{-3}	0.19
	Clay	7.73×10^{-2}*	3.74×10^{-2}	0.11
	SOM	3.08×10^{-1}**	4.55×10^{-2}	0.06
K_L	Constant	-1.88×10^{-1}*	5.28×10^{-2}	-
	M3-Fe	2.66×10^{-4}**	8.78×10^{-5}	0.09
	M3-Al	4.63×10^{-5}**	1.10×10^{-5}	0.04
	SOM	1.88×10^{-4}*	7.61×10^{-4}	0.31
	pH	1.42×10^{-2}**	5.05×10^{-3}	0.08
K_F	Constant	-3.66**	9.19×10^{-1}	-
	M3-Fe	5.50×10^{-3}*	2.06×10^{-3}	0.35
	SOM	2.67×10^{-2}*	1.11×10^{-2}	0.71
n	Constant	-6.08**	2.08	-
	M3-TP	-5.01×10^{-3}*	4.66×10^{-3}	0.11
	M3-Al	2.53×10^{-3}**	8.34×10^{-4}	0.20
	SOM	-6.62×10^{-2}*	3.33×10^{-2}	0.06
	pH	6.49×10^{-1}**	1.80×10^{-1}	0.16

*Significant at < 0.05 probability level.

**Significant at < 0.01 probability level.

[€]q_{max} and K_L are maximum adsorption capacity and adsorption constant, both estimated from the nonlinear Langmuir model; K_F and n are determined from Freundlich model-fitting.

4.5. Conclusions

This study is the first to assess P adsorption for natural and managed soils in the province of Newfoundland and Labrador, with a unique added focus on the state of lands converted to agricultural use. The long-term agricultural field had developed an Ap horizon more or less in line with agricultural soils elsewhere, with the potential to act as both sink and source for P. On the other hand, the soils under the recent land-use conversion have been shown to be significant P sinks. Thus, while over the short term, a newly converted soil might act as a sink for P this can lead to long-term legacy P accumulation that might become available later as soil organic matter and soil chemical and physical parameters shift under the effect of repeated agricultural practices aimed at controlling pH and fertility. These disparities between new and old agricultural sites in the boreal ecosystem point to the need for distinct management and critically distinct management decision approaches to P fertilisation. Thus, future soil fertilisation research here and in similar scenarios across the boreal ecosystem must be carefully designed and interpreted to account for the variability in P kinetics.

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4.7. Supplementary Material

Table S4.1. Physicochemical soil characteristics of forested and managed SJRDC and CAFD soil horizons.

Management & Location	*Horizon*	Texture	Clay	Silt	Sand	SOM	TC	TN	pH	EC	M3-Ca	M3-K	M3-P	M3-Al	M3-Fe	Al:Fe	P/(Al+Fe)
			----------%----------						–	µS cm^{-1}	----------mg L^{-1}----------					---Ratio---	
Forested-SJRDC	LFH	*NA	NA	NA	NA	47.2	29.8	1.3	5.24	216	1486	282	60.5	1409	368	3.8	0.033
	B	Loam	17	46	38	13	9.1	0.54	4.91	142	452	67	13.7	1765	160	11.0	0.006
	BC	Loam	10	41	50	5.4	5.2	0.32	5.15	41	27	19	4.5	1972	84	23.6	0.002
Managed-SJRDC	Ap	Loam	17	40	43	10.9	7.9	0.56	6.07	168	2155	90	57	1405	169	8.3	0.033
	B	Sandy loam	7	38	55	6.5	4.5	0.28	6.04	61	844	412	8.1	1850	96	19.3	0.004
	C	Sandy	6	33	61	1.3	1.2	0.09	6.06	33	118	14	67.7	1713	73	23.4	0.034
Forested-CAFD	LFH	NA	NA	NA	NA	22.7	29.4	0.58	3.36	171	854	315	74.6	983	300	3.3	0.058
	E	Silty loam	9	55	36	3.3	1.7	0.06	3.73	86	24	28	13.3	1106	266	4.2	0.009
	B	Sandy loam	7	33	60	3.3	3.2	0.14	5.18	22	22	13	2	1803	94	19.2	0.001
	BC	Sandy loam	2	28	70	1.2	0.76	0.04	5.39	15	2	7	5.1	1887	32	59.2	0.002
Managed-CAFD	Ap	Sandy loam	8	36	56	3.6	2.4	0.13	4.79	72	41	79	40.8	1799	99	18.2	0.019
	E	Silty loam	6	46	48	0.8	0.28	0.02	5.34	25	11	47	19.2	1729	52	33.1	0.010
	C	Sandy	4	20	76	0.4	0.22	0.02	5.68	18	11	30	74.5	1539	44	34.8	0.042

*Not applicable (NA), M3-Ca, M3-K, M3-P, M3-Al and M3-Fe represent Calcium, Potassium, Phosphorus, Aluminium, and Iron extracted by Mehlich 3 solution and analyzed with ICP-OES, respectively. P/(Al+Fe) was computed from P, Fe, and Al concentrations expressed in mmol kg^{-1}.

Table S4.2. Mineralogical composition of forested and managed SJRDC and CAFD soils.

Management & Location	*Horizon*	Mineral phases						
		Quartz	*Albite*	*Muscovite*	*Clinochlore*	*Kaolinite*	*Anorthite*	*Berlinite ($AlPO_4$)*
Forested-*SJRDC*	LFH	+	+	+	+	-	+	-
	B	++	+	-	+	-	-	-
	BC	++	+	+	+	+	-	-
Managed-*SJRDC*	Ap	++	+	+	+	-	-	-
	B	++	+	-	++	+	+	-
	C	++	++	+	+	-	-	-
Forested-*CAFD*	E	+++	+	-	-	-	-	+
	B	+++	++	+	+	-	+	-
	BC	++	+	-	-	-	+	+
Managed-*CAFD*	Ap	++	++	+	+	-	+	-
	E	++	+	-	+	-	+	+
	C	++	+	-	+	-	-	-

+++ abundant, ++ moderately abundant, + slightly abundant, - absent

Adsorption tests; technical considerations

The empirical maximum P adsorption was obtained from adsorption isotherms for initial P concentrations ranging from 0-1000 mg P L^{-1}. The study of Väänänen et al. (2008) did not reach the expected q_{max} as it used P concentrations of only 0-100 mg P L^{-1}. Väänänen et al. (2008) also argued that laboratory measurement might underestimate the P adsorption by E horizons. While Al and Fe contents are not altered during handling, mineralization of SOM can increase available P (Väänänen et al., 2008).

Nevertheless, similarly to this study, the adsorption isotherm parameters in other studies (Nobile et al., 2018; Väänänen et al., 2008; Villapando & Graetz, 2001; Wang et al., 2016; Warrinnier et al., 2019) were mainly explained from the perspective of chemical processes. While most adsorption might occur instantaneously (Guedes et al., 2016; Novak &

Adriano, 1975), adsorption continues slowly after the initial contact. Moreover, the adsorption profile depends on the soil's changeable mineral and organic matter makeup. A 24 h contact time was employed for this experiment (Väänänen et al., 2008) to allow for a realistic contact duration while also minimizing the impact of changes in soil's parameters, especially for SOM, during the incubation. Longer contact time may be likely not warranted as soil enters an equilibrium state where both sorption and desorption occur.

In general, the q_{max} of the tested Nfld soil were higher than those observed in other P adsorption studies, which may be attributed to; (1) differences in the electrolyte solution (buffering solution; *i.e.* $CalCl_2$ vs KCl) (Dari et al., 2015; Kruse et al., 2015), (2) difference in models (linear vs nonlinear), (3) differences in soil parent materials, (4) differences in background or legacy P level (Nair & Harris, 2014), (5) adsorption parameters (contact time, agitation speed, and initial concentrations) (Kruse et al., 2015), and (6) in the use of microbial inhibitors (P. S. Nair et al., 1984). For the absorption experiments, I employed 0.01M KCl electrolyte solution (Dari et al., 2015; Ige et al., 2005; P. S. Nair et al., 1984) while other studies (Anghinoni et al., 1996; Dalal, 1977; Jalali & Jalali, 2016; P. S. Nair et al., 1984) employ 0.01M $CaCl_2$. The decision to use 0.01M KCl versus $CaCl_2$ is recommended to prevent precipitation of P as $CaPO_4$ (Börling, Otabbong, & Barberis, 2001; P. S. Nair et al., 1984).

Multivariate analysis for determining the relationship between soil properties and P adsorption parameters

Principal component analysis (PCA) was employed using correlation matrix values to visualize the loading contribution of four adsorption and fourteen soil parameters and

observe the directional relation of the soil horizons according to the selection criteria. Accordingly, the PCA of 13 soil horizons representing SJRDC and CAFD explains 45%, 17%, 16%, and 9% variation in PC1, PC2, PC3, and PC4, respectively (Table S4.3). The first PC was positively loaded with SOM, TC, TN, EC, Freundlich adsorption capacity (K_F) and Mehlich-3 extractable cations (mainly Ca, K, and Fe), whereas Mehlich-3 extracted Aluminium (M3-Al) and median depth were negatively loaded in PC1 (Table S4.3). Thus, PC-1 may be interpreted as the organic and cationic factors, which were affected by acidity and soil horizon. The second principal component (PC2) was positively loaded with Freundlich adsorption intensity (n), Langmuir adsorption rate (K_L), and soil pH while negatively loaded with silt content (Table S4.3). The second component may be interpreted as adsorption-correlated factors but impacted by soil texture.

Similarly, the third component was negatively loaded with M3-P and clay content. Therefore, the third principal component affected by the soil P level and clay content. The maximum adsorption capacity (q_{max}) was positively loaded in PC4. PC1 defined the importance of soil organic matter in the soil cation exchange capacity and P adsorption. Also, it is possible to claim that aluminium was the dominant species responsible for P adsorption in Podzol soil as per the PC1 loading.

Table S4.3. Principal components (PC) and component loadings (correlation) extracted from 18 soil physicochemical variables for soil horizons; bolded values within component loading were used to interpret the PC.

Variables	*Principal Components*			
	PC 1	PC 2	PC 3	PC 4
M3-Ca (mg kg^{-1})	**0.74**	0.21	0.04	0.48
M3-K (mg kg^{-1})	**0.86**	0.04	-0.41	-0.16
M3-P (mg kg^{-1})	0.35	0.14	**-0.76**	0.30
M3-Fe (mg kg^{-1})	**0.93**	-0.17	-0.12	-0.17
M3-Al (mg kg^{-1})	**-0.60**	0.47	0.50	0.01
q_{max} (mg g^{-1})	0.30	-0.08	0.19	**0.67**
K_L (L mg^{-1})	0.44	**0.68**	0.44	-0.26
K_F (L mg^{-1})	**0.69**	0.52	0.11	-0.09
n (L mg^{-1})	0.13	**0.66**	0.58	-0.33
Median depth (cm)	**-0.72**	0.40	-0.33	0.05
Clay (%)	**0.53**	-0.25	0.48	0.45
Silt (%)	0.37	**-0.62**	0.58	-0.18
Sand (%)	-0.48	0.56	**-0.62**	-0.03
SOM (%)	**0.93**	0.30	-0.11	-0.10
TC (%)	**0.90**	0.12	-0.29	-0.20
TN (%)	**0.93**	0.33	0.05	0.05
pH	-0.37	**0.70**	0.22	0.50
EC (μS cm^{-1})	**0.97**	-0.03	-0.01	0.13
Eigenvalues	8.15	3.11	2.79	1.57
Variance proportion	45.30	17.30	15.50	8.71
Cumulative variance	45.30	62.61	78.10	86.81

Chapter 5. PHOSPHORUS SORPTION CAPACITY ASSESSMENT AND ITS RELATIONSHIPS WITH SOIL PROPERTIES UNDER LONG-TERM MANAGED PODZOLIC SOILS IN NEWFOUNDLAND

5.1. Abstract

Repetitive and excessive use of inorganic fertilizers has long been recognized to lead to phosphorus accumulation in agricultural soils. This can pose environmental risks if the soil's phosphorus storage capacity is not well understood and considered when planning nutrient management. I investigated the P adsorption capacity in the surface (0-20 cm) and subsurface (20-40 cm) of long-term managed soils in the eastern Newfoundland (Nfld), Canada through batch adsorption using two P concentrations, 150 and 500 mg P L^{-1}. Basic soil properties were used as proximate indicators for P adsorption through linear correlations and multiple regression models. The surface soils had significantly higher available P, total P, soil organic matter (SOM), iron (Fe), calcium (Ca), potassium (K), electrical conductivity (EC), silt, and clay contents, while aluminium (Al) and sand were higher in the deeper soil ($p<0.01$). The soil pH was comparable (~6.3) for both depths ($p = 0.66$) but the deeper soil layers had a significant higher P adsorption capacity when tested with the 500 mg PL^{-1} solutions ($p = 0.02$). A P concentration of 500 mg P L^{-1} can be used to assess the single-point P adsorption capacity of Nfld or similar Podzols. Soil organic matter, Al, and total P may be employed to predict P adsorption capacity and thus employed

to develop testable hypotheses for the development of environmentally and economically viable P management strategies for acidic soils in boreal regions.

Keywords: Phosphorus adsorption capacity, phosphorus, managed Podzols, Newfoundland

5.2. Introduction

Phosphorus (P), critical for metabolic regulation of all living cells, is a non-renewable resource (Scholz et. al, 2013). Following World War II, and with increased access to fossil fuel energy (Dery, 2007), P has been heavily mined of which ~82% is used as fertilizer (Smil, 2000). Large and repetitive applications of P and nitrogen (N) mineral fertilizers, especially after 1970's, improved soil productivity and increased crop yields (Cordell & White, 2013, 2014). Additionally, the expansion of dairy industries increased the availability of manure as a source of plant nutrients like nitrogen and P (Barnett, 1994; Vriesema, 1984).

During the Green Revolution (IFPRI, 2002) excessive and repetitive application of fertilizer led to P accumulation (*i.e.* legacy P) in agricultural and pasture soils (Roy et al., 2017). Since then, and with continued P fertilizer applications, this build up has become a major agronomic and environmental concern (Nair, 2014). For example, excessive application of manure to Dutch fields in the 1980's led to an average legacy P of 2,050 kg P ha^{-1} (Schoumans, 2015). Also, in Germany, an average of 1,100 kg P ha^{-1} was reported in 2010 (Fischer et al., 2017). In Newfoundland (Nfld), Canada, lands converted from boreal forests to agricultural use in the early and mid 20^{th} century received manure repeatedly to maintain fertility. The large application of manure to satisfy crop N requirements resulted in P accumulation in the soils (Qian et al., 2004). The P accumulated

in agricultural soils is either strongly fixed by clay minerals and sesquioxides of Al, Fe, and Ca (Cade-Menun et al., 2000; Eriksson et al., 2015; Eriksson et al., 2016; Read & Campbell, 1981; Roy et al., 2017) or labile P (Arruda Coelho et al., 2019). Based on the soil properties, mainly pH and organic matter, the non-labile P could transform to labile and then to available P (Costa et al., 2016). Making legacy P available to plants reduces the need for further P inputs. On the other hand, P build-up can pose environmental problems associated with erosion or leaching to the groundwater (Haygarth et al., 2014; Väänänen et al., 2008), mainly resulting in water pollution (*i.e.* eutrophication) (King et al., 2015).

The accumulation of P in soils is related to soil properties and its buffering capacity, and field management history (Eriksson et al., 2016; Luo et al., 2017; Roy et al., 2017). For example, the Ap horizons (plow layer) of long-term managed Podzols in eastern Nfld have a high P adsorption capacity that strongly correlates with the soil Al concentrations (Chapter 4). Long term (30 years) intensely fertilized acid soils in Mato Grosso, Brazil, release 14 kg of legacy P ha^{-1} annually; however, 75% of the legacy P may be inaccessible to plants despite the decline of P sorption by the soils (Roy et al., 2017). Some clayey soils, despite excessive P fertilizer applications, still exhibit high P adsorption capacities (Roy et al., 2017). Century-old managed Denmark arable soils have higher annual P accumulations (up to 25 kg P ha^{-1}) in surface soils (0-25 cm) and a higher total P mobility to depths of up to 75 cm than adjacent deciduous forest soils (Rubæk et al., 2013).

It is thus necessary to understand P dynamics in long-term managed fields to ensure efficient utilization of limited phosphate reserves and provide environmental stewardship while satisfying crop requirements (Roy et al., 2017). Agronomic and environmental analytical techniques and indices have been developed to assess the P status of soils under

different management regimes. Among these, soil P storage capacity (SPSC) is used as a proxy for assessing and predicting the P storage and release capacities of soils over short or long terms after receiving manure or mineral fertilizers (Nair & Harris, 2014). Soil tests for P (*P-tests*) such as Mehlich-1, Mehlich-3, or others, initially developed for agronomic purposes have recently also been employed for environmental risk assessments (Howard, 2006; Radcliffe & Cabrera, 2007; Wuenscher et al., 2015). For this P saturation ratios (PSR) are calculated as the molar ratio of P to Al or Al plus Fe (Benjannet, Khiari, et al., 2018; Dari et al., 2015; Maguire & Sims, 2002; Nair, 2014; Nair & Harris, 2014). The P adsorption of various soils has thus been well studied to determine soil fertility and assess environmental risks (Nobile et al., 2018; Jalali & Jalali, 2016; Muwamba et al., 2016; Wang et al., 2016). However, site-specific P adsorption studies are required given regional specificity of soil and environmental conditions (Daly et al., 2015). Phosphorus adsorption in long-term managed boreal soils, particularly the variability in adsorption by the depth, has not yet been thoroughly investigated for Nfld soils.

Thus, this study aims to assess (1) the residual P adsorption capacity of the surface (0-20 cm) and subsurface (20-40 cm) long-term managed soils, and (2) the amount of legacy P and the soil characteristics that best correlate to P adsorption capacity. This information is critical for the development of sustainable nutrient management plans and a data informed decision support system for the planned agricultural expansion in the boreal regions, such as Newfoundland and Labrador.

5.3. Materials and Methods

5.3.1. Site Description

St. John's Research and Development Centre, Agriculture and Agri-food Canada, fields (47.56° N, 52.71° W) have been farmed for ~150 to 160 years, mainly for perennial forage production followed by crop field trials in the last 50 to 80 years (Cordeiro et al., 2019; Spaner et al., 2000; Spaner et., 2001). The site (~28 hectares) has 23 unequally partitioned fields, which had been under deep plough farming, mainly for perennial forage production for dairy farms in the Avalon Peninsula (M. Cordeiro et al., 2019), since the 1860s. On the other hand, the soil quality benchmark site described in a field report indicated that some of the fields were converted to agriculture in 1937 (Woodrow et al., 1996). These converted fields received 227 kg ha^{-1} of 6-12-12 fertilizer and an unknown amount of manure, as often as 2 to 3 times per year, for the first 30 years. Also, during the same period, the fields received three applications of limestone at the rate of 4 Mg ha^{-1} (Woodrow et al., 1996). Since 1949, the fields have been used for field trials for forage, annual crops, and vegetables. Most fields were managed under timothy (*Phleum pratense*), red clover (*Trifolium pratense*) and alsike clover (*Trifolium hybridum*) mixtures in rotation with research crops and have received various rates of mineral fertilizer or manure and lime applications. Since 1949, forage fields yielded 1 to 2 cuts annually; silage production and earlier harvesting has allowed for 2 to 3 cuts per year in recent years. Another field, rocky and with poor drainage, was allowed to naturally regrow to forest in the 1970's to early 1980's with black spruce (*Picea mariana*), mountain ash (*Sorbus americana*), and serviceberry (*Amelanchier bartramiana*).

5.3.2. Soil Sampling

Soil samples were collected from the 23 *managed* fields in November 2017. Proportional to the field size, 3 to 5 sampling locations per field were randomly selected. From each location, triplicated cores were collected at 1-metre intervals from 0-20 cm and 20-40 cm depths. Thus, for each field a variable number of 9 to 15 same-size samples of about 300 g each were collected in clean bucket for each depth and composited to produce one sample per depth for each field (46 samples). Eventually an aliquot of about 1 L of fresh soil was transferred into 1.5 L polyethylene Ziploc bags and transported to the laboratory.

5.3.3. Sample Handling, Processing, and Analysis

All soil samples were stored at -10 °C until analysed. The moisture content was determined gravimetrically (oven-dried at 105 °C for 24 h) within 4-6 h of sampling, before freezing the samples. Before testing, the frozen soil samples were thawed at 4 °C for 72 h, followed by air-drying for 3 to 5 d in a temperature-controlled room (~35 °C with air movement) and then passed through a 2 mm sieve.

Soil samples were analyzed for (1) soil organic matter (SOM) based on the loss-on-ignition method at 430 °C heated for 6 h (Jones, 2001; Kalra & Maynard, 1991); (2) moisture content (MC) determined by drying field-fresh sample in the forced-air oven at 105 °C for 24 hr (Kalra & Maynard, 1991); (3) pH and EC measured in 1:2 soil to double distilled water (Carter & Gregorich, 2008); (3) particle size distribution was determined using hydrometer method (Carter & Gregorich, 2008); (4) mineralogical analysis was carried out on a Rigaku Ultima-IV Powder X-Ray Diffractometer (XRD) (Rigaku Corporation, Tokyo,

Japan) at 2Theta theta^{-1}, 40kV and 44mA; (5) soluble reactive (available) P was determined in Mehlich-3 (M3), 1% citric acid (CA), and deionized water (H_2O) extract (1:10 soil to solution ratio) using ascorbic acid method as described by Murphy and Riley (1962) and modified by Watanabe and Olsen (Watanabe & Olsen, 1965); and (6) total P and micro and macronutrients in Mehlich-3 extract were determined using a Prodigy High Dispersion ICP-OES (Teledyne Leeman Labs, Manson, USA).

5.3.4. Adsorption Experiment

For all 46 samples, representing *D1* and *D2* soils, single-point P adsorption capacity tests were performed (Börling et al., 2001) using initial concentrations of 150 and 500 mg P L^{-1}. These initial P concentrations were identified from the calibrated adsorption isotherm experiment employed in Chapter 4. Briefly, a 2 ± 0.01 g sample of air-dried soil was added to a 125 mL Erlenmeyer flask and saturated with 20 mL of 0.01M KCl solution containing either 150 or 500 mg P L^{-1}. The soil-solution mixture was agitated for 1 h on an end to end shaker followed by equilibration at room temperature (~20 °C) for 22 h and eventually re-agitated for another 1 h (Väänänen et al., 2008). The soil-solution was filtered through 0.45 µm paper filters to collect the filtrate (Bache & Willims, 1971; do Carmo Horta & Torrent, 2007; Ige et al., 2005; Jalali & Jalali, 2016). The equilibrium P in the filtrate was determined using the ascorbic acid method as described by Murphy and Riley (1962) and modified by Watanabe and Olsen (Watanabe & Olsen, 1965). All experiments were conducted in triplicate.

The P adsorption protocol used is similar to that employed in other studies (Bache & Willims, 1971; do Carmo Horta & Torrent, 2007; Ige et al., 2005; Jalali & Jalali, 2016; Olsen & Watanabe, 1957) except that microbial inhibitors like toluene or chloroform were not used as they increase dissolved P in solution through lysis of microbial cells (Sims & Hodges, 2000). The amount of phosphate adsorbed at equilibrium (qe) was calculated using Equation (5.1):

$$q_e = \frac{(C_i - (C_e - C_o) * V}{m} \qquad \textit{Equation (5.3)}$$

Where: q_e (mg g^{-1} of soil) is the amount of P adsorbed at equilibrium; C_i, C_e, and C_o are the initial, equilibrium, and labile P concentrations (mg L^{-1}), respectively; V is the volume of the solution in L and m is the oven-dry soil mass (g) (Chen, 2015).

5.3.5. Statistics

Descriptive and explanatory statistics were carried out using Microsoft Excel (2018), PAST3 (Hammer et al., 2001), and Origin(Pro) vs.2019 (OriginLab Corporation, Northampton, MA, USA., 2019). Pearson correlations and principal component analyses (PCA) based on correlation matrices were performed to identify the relationship between point adsorption capacity and soil properties. A one-way ANOVA followed by a posthoc Tukey's test was applied to compare the means of the adsorption capacity and soil properties between the fields and depths. Additionally, stepwise multiple regressions were further employed to assess the statistical relationship between point P adsorption capacity and soil variables.

5.4. Results and Discussion

5.4.1. Baseline Soil Characteristics

The *D1* soils were classified as either silty loam or loam, whereas the *D2* soils were mainly classified as loams. The *D1* soils have a median pH of 6.3, EC of 239 µS cm^{-1}, clay content of 18%, silt content of 50%, sand content of 32%, and SOM of 12% (Table 5.1). The *D2* soils have a median pH of 6.3, EC of 148 µS cm^{-1}, clay content of 16%, silt content of 42%, sand content of 43%, and SOM of 9% (Table 5.2).

The median contents of clay, silt and SOM in *D1* soils were significantly greater than for *D2* soils ($p<0.001$) while the reverse was observed for Al and sand content (Table 5.3). However, the XRD mineralogical analysis showed similar mineral phases in *D1* and *D2* soils except for Berlinite ($AlPO_4$), which was only detected in *D1* soils (Table 5.4). Differences in soil characteristics between the two depths could be due to the management history as most of the soil-plant interactions and tillage, happened in the top 15-20 cm of the soil. Additionally, the *D1* soils may have an accelerated biomass turnover resulting in higher SOM which also increases moisture retention and EC. The *D1* soils, with higher SOM, had significantly higher EC than *D2* soils (Table 5.3). The SOM is the source of carboxyl and phenolic acids the largest contributors to cations exchange capacity in the soil (Wang & Huang, 2001). Remarkably, the median pH of the *D1* and *D2* soils was not significantly different ($p=0.66$). The minor pH increase in the *D2* could be due to calcium leaching from *D1* into the subsurface (Conyers et al., 2003).

Median soluble reactive P concentrations of 36.5, 131.2, and 0.9 mg P L^{-1} in *D1* soils and 12.8, 90.1, and 0.7 mg P L^{-1} in *D2* soils were measured spectrophotometrically in the

Mehlich-3, 1% citric acid, and water extract, respectively (Table 5.1 and Table 5.2). The soluble reactive water-P and Mehlich-3-P concentrations were significantly higher in *D1* than *D2* soils (Table 5.3). The 1% citric acid (CA) extracted more P from *D1* than *D2* soils (Table 5.3); the 1% citric acid solution can extract more organic and inorganic P compared to water and Mehlich-3 solution (Wei et al., 2010). The CA-P in the *D2* soils might signal the vertical mobility of P due to long-term management and/or higher fertilizer application (Ojekami, 2011; Rubæk et al., 2013), but also an effect combined with the natural podsolization mechanisms under the boreal climate. Also, the median of total P, K, Ca, and Fe extracted by Mehlich-3 from *D1* soils were significantly greater than for *D2* soils ($p<0.001$) while for Al the trend was reversed ($p<0.001$) (Table 5.3). The differences between *D1* and *D2* physicochemical soil properties can be attributed to the long-term recurring application of manure or mineral fertilizers, liming, and cropping (Conyers et al., 2003; Johnston et al., 2014). Previous studies (Allen & Mallarino, 2006; Liu et al., 2014; Whalen & Chang, 2001) reported increased available or total P in surface soils of long-term managed fields. The *P-tests* can be used to assess the effect of long-term management on P pools (Allen & Mallarino, 2006). Furthermore, in Lethbridge, Alberta, Canada, experimental plots that received various rates of manure for 16 years showed P build-up in surface (0-15 cm) soils and vertical mobility of available and total P (Whalen & Chang, 2001).

While the surface (*D1*) soils in this study have higher SOM, silt, clay, and lower Mehlich-3-P compared to soils in the nearby Nova Scotia, Prince Edward Island, and New Brunswick provinces of Canada (Benjannet, Nyiraneza, et al., 2018), they were overall

comparable. Differences could be attributed to the history of the managed sites, soil mineral contents, and the rates of manure application (Cordeiro et al., 2019).

The P build-up could be due to various factors, including (1) over application of fertilizer by not conforming to the "law of minimum" (Von Liebig, 1855), (2) excessive application of manure to satisfy N requirements (Qian et al., 2004; Shober, 2006), and (3) nature of the soil properties or low fertilizer responses (high P fixation) (Grant et al., 2005). However, there is limited knowledge on whether these soils had reached their P adsorption capacity due to long-term management.

Table 5.1. Physicochemical characteristics of D1 (0-20cm) soils.

Field	*Clay*	*Silt*	*Sand*	*MC*	*SOM*	*pH*	*EC*	*H_2O-SrP*	*CA-SrP*	*M3-SrP*	*M3-Ca*	*M3-K*	*M3-P*	*M3-Fe*	*M3-Al*
	----------%----------					-	µScm^{-1}	----------mg kg^{-1}----------							
F1	20.7	52.4	26.9	49.7	10.6	6.9	238	0.7	67.4	15.6	3598	129	20.7	215	1380
F2	20.7	50.1	29.2	55.4	12.4	6.6	183	0.7	110.4	22.4	2753	281	28.1	192	1478
F3	16.7	53.7	29.6	42.0	12.7	6.6	273	1.1	111.4	25.6	3098	243	30.6	150	1344
F4	18.7	55.7	25.6	66.4	15.0	6.2	243	BDL	103.5	26.8	2892	124	32.2	225	1327
F5	16.7	51.7	31.6	44.9	12.7	6.5	239	0.9	147.7	42.5	2958	264	46.4	197	1362
F6	18.7	52.1	29.2	44.9	12.4	6.4	197	1.0	147.2	38.8	2485	186	41.5	184	1404
F7	20.7	51.2	28.2	41.2	9.1	6.6	347	1.9	383.9	123.3	3297	359	118.0	260	1338
F8	16.7	53.2	30.2	48.8	11.3	6.6	230	1.0	131.2	33.5	2931	261	37.8	209	1321
F9	14.7	51.9	33.4	69.3	15.8	6.7	280	BDL	119.4	27.8	3894	177	35.4	199	1328
F10	20.0	52.4	27.6	39.4	10.6	6.2	166	0.8	165.2	40.9	2105	109	40.6	196	1396
F11	16.0	42.4	41.6	59.8	16.3	6.2	190	1.2	114.1	33.5	2187	130	41.3	190	1410
F12	18.0	46.4	35.6	39.2	10.2	6.4	234	0.8	158.3	46.0	2850	177	49.4	199	1299
F13	18.0	45.2	36.9	35.1	9.2	6.3	166	0.9	247.5	62.1	2094	165	59.9	210	1367
F14	19.0	46.2	34.9	39.6	12.2	6.0	240	BDL	77.4	12.8	2322	54	17.3	178	1444
F15	20.0	44.4	35.6	42.3	10.9	6.3	297	0.8	187.3	40.2	2164	306	42.7	165	1453
F16	22.0	44.4	33.6	42.2	12.1	6.5	240	0.8	119.6	36.5	2584	186	40.5	190	1444
F17	20.0	50.4	29.6	66.0	12.9	5.0	88	BDL	18.1	1.0	447	114	6.8	219	1949
F18	15.0	46.2	38.9	53.5	15.3	5.6	322	1.4	366.4	117.5	2051	276	130.7	162	1513
F19	13.0	46.2	40.9	51.4	14.6	6.4	419	1.2	55.9	21.9	3244	221	30.3	171	1177
F20	16.7	53.6	29.8	83.6	20.0	6.1	338	0.8	157.6	26.6	2713	114	34.5	159	1482
F21	16.7	43.6	39.8	40.8	12.1	6.1	137	0.8	382.9	87.1	2221	166	86.6	237	1509
F22	18.7	43.6	37.8	36.9	11.7	6.2	262	1.1	365.2	94.0	2338	206	94.0	197	1474
F23	16.7	63.6	19.8	70.4	9.2	6.1	175	0.5	88.3	39.4	1910	76	54.9	364	1092
Average	18.0	49.6	32.4	52.4	12.6	6.3	239	1.0	166.3	44.2	2571	188	48.7	203	1404
STD	2.3	5.0	5.5	17.5	2.6	0.4	75	0.3	108.3	32.0	701	78	30.8	44	155
Median	18.0	50.4	31.6	44.9	12.2	6.3	239	0.9	131.2	36.5	2584	177	40.6	197	1396

Moisture content (MC), soil organic matters (SOM), electrical conductivity (EC); *H_2O-SrP, CA-SrP, and M3-SrP represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis;* M3-Ca, M3-K, M3-P, M3-Fe, and M3-Al are calcium (Ca), potassium (K), phosphorus (P), iron (Fe), and aluminium (Al) analysed by ICP-OES in Mehlich-3 (M3) extract, below the detection limit (BDL) of 0.01 mg P kg^{-1} which varies for the different tests.

Table 5.2. Physicochemical characteristics of D2 (20-40cm) soils.

Field	Clay	Silt	Sand	MC	SOM	pH	EC	H2O-SrP	CA-SrP	M3-SrP	M3-Ca	M3-K	M3-P	M3-Fe	M3-Al
	----------%----------					-	µScm-1	----------mg kg-1----------							
F1	*16.7*	*40.1*	*43.2*	*38.0*	*8.5*	*6.9*	*130*	*BDL*	*48.2*	*3.8*	*2207*	*34*	*6.5*	*189*	*1650*
F2	14.7	37.7	47.6	36.1	8.9	6.4	159	BDL	78.6	6.1	1559	60	8.8	144	1809
F3	*14.7*	*37.7*	*47.6*	*32.7*	*9.0*	*6.6*	*162*	*BDL*	*82.7*	*12.8*	*1857*	*45*	*15.7*	*108*	*1613*
F4	12.7	41.7	45.6	37.0	10.7	6.2	83	0.7	68.6	6.6	1437	39	9.5	186	1677
F5	*14.7*	*41.7*	*43.6*	*34.9*	*10.2*	*6.6*	*148*	*BDL*	*90.1*	*12.8*	*1975*	*81*	*15.1*	*146*	*1593*
F6	16.7	54.4	28.9	38.9	10.8	6.4	151	BDL	117.3	14.9	2193	77	17.8	168	1602
F7	*18.7*	*48.8*	*32.5*	*36.0*	*10.1*	*6.6*	*331*	*0.9*	*314.4*	*82.5*	*2936*	*239*	*78.7*	*207*	*1406*
F8	15.7	50.2	34.2	42.3	12.0	6.6	163	BDL	119.0	22.6	2628	105	25.5	189	1388
F9	*12.7*	*35.2*	*52.2*	*37.0*	*10.1*	*6.5*	*125*	*BDL*	*60.6*	*5.1*	*1675*	*52*	*8.6*	*137*	*1786*
F10	16.0	40.4	43.6	33.4	7.2	6.3	100	BDL	144.0	30.2	1538	105	30.9	175	1515
F11	*14.0*	*36.4*	*49.6*	*39.4*	*8.5*	*6.4*	*80*	*BDL*	*61.1*	*8.6*	*814*	*28*	*12.1*	*136*	*1675*
F12	16.0	41.2	42.9	32.4	10.3	6.2	196	BDL	126.0	22.3	2100	64	24.0	144	1482
F13	*16.0*	*43.2*	*40.9*	*29.3*	*8.8*	*6.3*	*126*	*BDL*	*185.0*	*47.5*	*1595*	*66*	*46.8*	*191*	*1506*
F14	15.0	42.2	42.9	35.6	11.3	5.9	164	BDL	60.3	4.9	1584	33	8.3	128	1667
F15	*14.0*	*36.4*	*49.6*	*31.7*	*9.0*	*6.2*	*228*	*BDL*	*138.6*	*28.5*	*1426*	*109*	*29.7*	*125*	*1603*
F16	18.0	42.4	39.6	37.9	9.4	6.5	172	0.7	101.2	14.2	2111	92	18.1	151	1619
F17	*17.0*	*42.2*	*40.9*	*34.2*	*7.9*	*5.1*	*50*	*BDL*	*37.6*	*1.9*	*98*	*48*	*6.2*	*120*	*2169*
F18	17.0	40.2	42.9	39.9	10.0	5.7	175	0.9	200.6	73.0	1499	140	78.3	116	1587
F19	*19.0*	*54.9*	*26.2*	*30.1*	*9.1*	*6.4*	*190*	*0.9*	*24.4*	*9.2*	*1903*	*78*	*13.8*	*178*	*1359*
F20	18.7	47.6	33.8	49.5	13.5	5.8	135	BDL	67.1	5.6	801	34	9.5	110	1731
F21	*13.7*	*36.6*	*49.8*	*28.8*	*7.6*	*6.1*	*83*	*0.2*	*289.1*	*31.5*	*1257*	*77*	*31.9*	*188*	*1782*
F22	15.7	38.6	45.8	30.0	8.8	6.1	146	0.4	247.5	47.1	1541	95	47.0	196	1656
F23	*12.7*	*51.6*	*35.8*	*24.1*	*2.7*	*6.0*	*61*	*0.2*	*27.5*	*10.9*	*490*	*24*	*14.8*	*296*	*1147*
Average	15.6	42.7	41.7	35.2	9.3	6.3	146	0.6	116.9	21.9	1618	75	24.2	162	1610
STD	*1.9*	*5.8*	*7.0*	*5.3*	*2.1*	*0.4*	*60*	*0.3*	*80.9*	*21.9*	*650*	*47*	*20.7*	*42*	*196*
Median	15.7	41.7	42.9	35.6	9.1	6.3	148	0.7	90.1	12.8	1584	66	15.7	151	1613

Moisture content (MC), soil organic matters (SOM), electrical conductivity (EC); *H_2O-SrP, CA-SrP, and M3-SrP represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis;* M3-Ca, M3-K, M3-P, M3-Fe, and M3-Al are calcium (Ca), potassium (K), phosphorus (P), iron (Fe), and aluminium (Al) analysed by ICP-OES in Mehlich-3 (M3) extract, below the detection limit (BDL) of 0.01 mg P kg^{-1} which varies for the different tests.

Table 5.3. One-way ANOVA comparison of the median values (n=23 for each depth) of D1 (0-20 cm) and D2 (20-40 cm) P adsorption capacities and soil characteristics.

Soil Variables	*Unit*	*Median Value*		*Kruskal-Wallis test*
		0-20 cm	20-40 cm	P-value
*Clay****	%	17.96	15.68	<0.001
*Silt****	%	50.44	41.72	<0.001
*Sand****	%	31.60	42.88	<0.001
*MC****	%	44.94	35.61	<0.001
*SOM****	%	12.24	9.05	<0.001
pH	-	6.29	6.33	0.660
*EC****	μScm^{-1}	238.58	147.78	<0.001
*H_2O-SrP****	mgL^{-1}	0.85	0.70	<0.001
*CA-SrP****	mgL^{-1}	131.24	90.10	<0.001
*M3-SrP***	mgL^{-1}	36.49	12.81	<0.001
*M3-Ca****	mgL^{-1}	2584.22	1584.17	<0.001
*M3-K****	mgL^{-1}	176.89	65.99	<0.001
*M3-P****	mgL^{-1}	40.59	15.65	<0.001
*M3-Fe****	mgL^{-1}	196.71	150.70	<0.001
*M3-Al****	mgL^{-1}	1395.79	1612.77	<0.001
PAC-150	mgg^{-1}	1.34	1.32	0.162
*PAC-500**	mgg^{-1}	2.27	2.74	0.020

Moisture content (MC), soil organic matters (SOM), electrical conductivity (EC); *H_2O-SrP, CA-SrP, and M3-SrP represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis;* M3-Ca, M3-K, M3-P, M3-Fe, and M3-Al are calcium (Ca), potassium (K), phosphorus (P), iron (Fe), and aluminium (Al) analysed by ICP-OES in Mehlich-3 (M3) extract, below the detection limit (BDL) of 0.01 mg P kg^{-1} which varies for the different tests. PAC-150 and PAC-500 represented a P adsorption capacity of soils treated with 150 mg P L^{-1} and 500 mg P L^{-1}, respectively, P-value $<0.001^{***}$, $<0.01^{**}$, <0.05*.

Table 5.4. Mineralogical composition of soil collected from D1 (0-20cm) and D2 (20-40cm) of SJRDC.

Field	*Depth (cm)*	*Quartz*	*Albite*	*Muscovite*	*Clinochlore*	*Kaolinite*	*Berlinite*
F3	0-20	++	+	+	+	+	+
F3	20-40	++	+	++	+	+	-
F23	0-20	++	+	++	+	+	-
F23	20-40	++	+	++	+	+	-

+++ abundant, ++ moderately abundant, + slightly abundant, - absent.

5.4.2. Phosphorus Adsorption Capacity

The initial concentration of the P in the solution, i.e., either 150 or 500 mg P L^{-1}, affected the measured adsorption capacity (Figure 5.2), in a similar way for both soil depths ($p = 0.16$) (Table 5.3 and Table S5.1, Supplemental Material). When the soils treated with an initial concentration of 150 mg P L^{-1}, the P adsorption capacities of *D1* and *D2* were not significantly different ($p = 0.16$). Nevertheless, when treated with 500 mg P L^{-1}, the adsorption capacity of *D2* soils (Table 5.3 and Table S5.1, Supplemental Material) was significantly greater than for *D1* soils, ($p = 0.02$) (Table 5.3 and Table S5.1, Supplemental Material). The higher SOM, Fe, and Ca contents in *D1* than *D2* soils and significantly higher Al in *D2* soils ($p<0.05$) are the main drivers for the P retention (Table 5.3). The higher P adsorption by *D2* soils may provide the benefit of controlling P loss to the groundwater, but further investigation is warranted to better understand the hydrological behaviour of P transport through macropores in Nfld Podzols (Williams et al., 2016). Agronomically, deep-rooted crops can access the accumulated P in the subsurface soils (Read & Campbell, 1981).

Specifically, fields F1 to F4, F6, F9, F11, F14, F17, and F20, mainly managed for forage purpose which have been receiving manure for long time and some limestone, had P adsorption capacities greater than the respective mean of all fields regardless of the depth and initial P concentrations. This may be explained by higher acidity ($pH<6.20$) and Al content compared to the remaining fields irrespective of the sampling depth (Table 5.3 and Figure 5.1.). One-way ANOVA demonstrated inconsistent P adsorption capacity of the fields, regardless of the depths and initial P concentration applied ($p = 0.05$) (Table 5.3 and

Figure 5.1.). Figure 5.1.a and 5.1b show the P adsorption capacities of *D1* and *D2* for 23 fields treated with 150 and 500 mg P L^{-1}, respectively.

Previous reports for non-calcareous soils (0-10 cm of grassland soils in Ireland) that have also suggested Al as the dominant P fixing agent have reported maximum P sorption capacities of 0.63 mg P g^{-1} (Daly et al., 2015); 0.38 mg P kg^{-1} were reported for long-term managed (35-40 years) top soils in central and southern Sweden (Börling et al., 2001). These values are 2 to 6 times lower than the adsorption capacities measured in SJRDC soils (Table 5.3). The Börling et al., (2001) report is procedurally relevant to the results as it employed a single-point P adsorption protocol and recommended a test solution of a concentration of 600 mg P kg^{-1}, similar to this study's 500 mg P L^{-1}.

The mechanism of P adsorption capacity in *D1* soils is linked to higher SOM, mineral content (mainly Al), and possibly metal-organic complexes (Olsen & Watanabe, 1957; Väänänen et al., 2008; Väänänen et al., 2007). Also, a high level of calcium was measured in *D1* soils (Table 5.1), which might precipitate P (Haynes, 1982), in addition to Al and Fe oxides (Szafranek & Skłodowski, 1999). Further study is required to evaluate the effect of long-term liming on P dynamics in the surface soils of SJRDC and similar fields.

The evidence for whether the SOM has negative or positive effect on P adsorption in the soil is inconsistent (Yang et al., 2019). The SOM is nevertheless a source of carboxyl anions (ROO^-) that attract P-retaining cations in addition to Fe and Al oxyhydroxides (Gustafsson, 2006; Warrinnier et al., 2019). In this study, the SOM had a strong linear correlation ($r = 0.47$ to 0.68) with the P adsorption capacity for *D1* and *D2* soils, regardless of the initial P concentration (Table 5.5). In the absence of detailed carbon chemical speciation, I cannot speculate to the mechanisms relating SOM to P adsorption in boreal

soils. Phosphorus adsorbed on metal-organic surfaces may easily be mineralized to available P forms depending on the soil pH (Haynes, 1982). The interaction between liming, P, and SOM in boreal soils requires further understanding to account for the P availability from the decomposition of the organic P pool as northern temperatures are expected to increase (Regelink et al., 2015; Verbeeck et al., 2017).

Despite their long-term management (150-160 years) history, the tested soils had lower extractable or plant-available P and a higher P adsorption capacity compared to some long-term managed tropical sulfic soils in Brazil and India (aeric Endoaquepts), or alkaline Manitoba and Ontario farmed soils (Bhattacharyya et al., 2015; Ige et al., 2005; Roy et al., 2017). On the other hand, tropical clay soils that received P fertilizers for three decades (Roy et al., 2017) had similar P retention trends regardless of the status of residual P. As often described, the Al and Fe levels in clay and Podzols are responsible for P adsorption (Bhattacharyya et al., 2015; Daly et al., 2015; Grand & Lavkulich, 2015; Roy et al., 2017). In this study, concentrations of Mehlich-3-P, citric acid-P, and water-extracted P were negatively correlated with P adsorption (Table 5.5), which confirmed the *D1* and *D2* soils to have a higher P retention capacity than reported elsewhere, with reactive Al oxides the most obvious driver (Bhattacharyya et al., 2015; Daly et al., 2015; Eriksson et al., 2015; Grand & Lavkulich, 2015; Roy et al., 2017; Szafranek & Skłodowski, 1999; Villapando & Graetz, 2001).

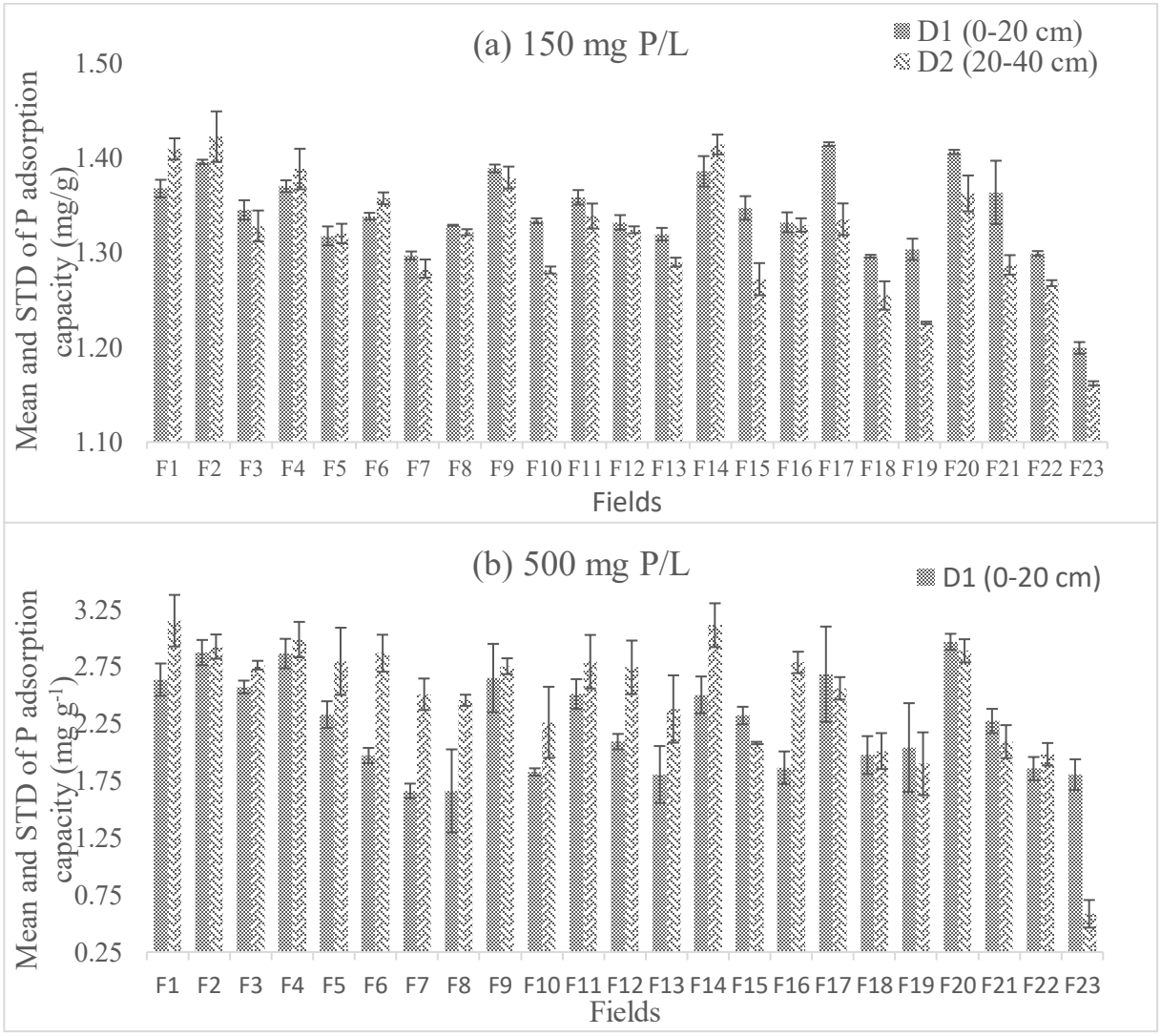

Figure 5.1. Phosphorus adsorption capacity of D1and D2 soils treated with (a) 150 mg P L^{-1} and (b) 500 mg P L^{-1} initial concentrations (n=3 per field per depth).

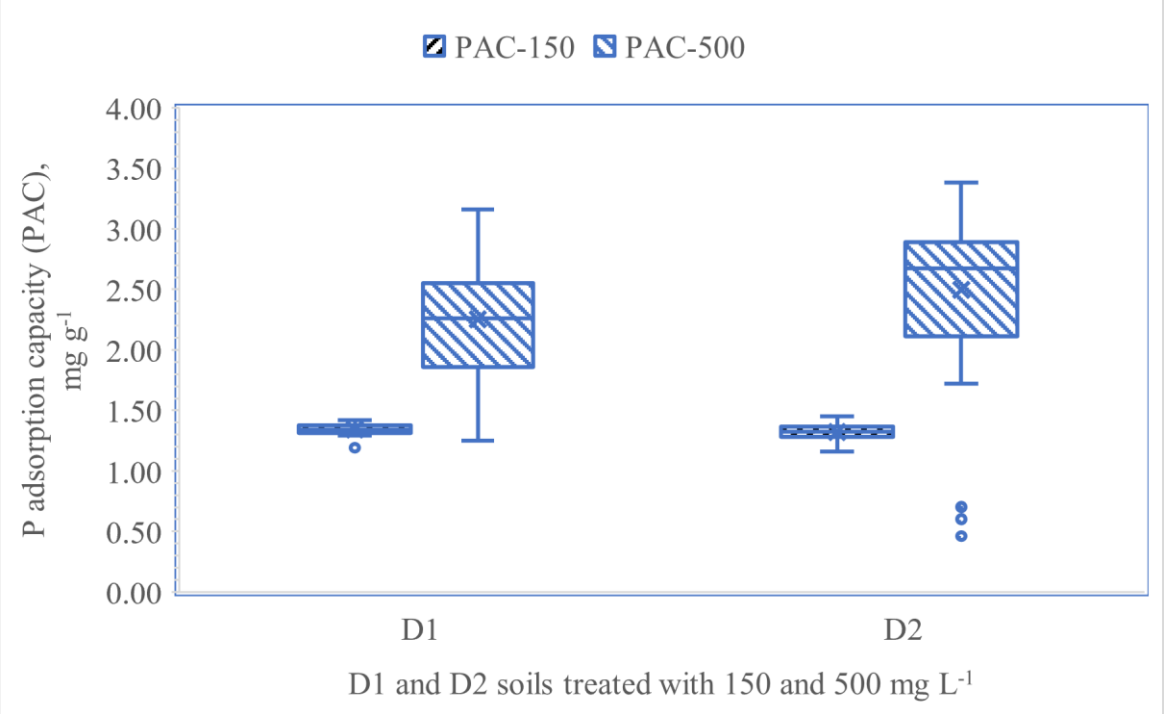

Figure 5.2. The pooled mean phosphorus adsorption capacity of D1 and D2 soils treated with 150 and 500 mg P L^{-1} initial (n = 23 soils for each depth, each sample triplicated).

5.4.3. Correlation of Point Phosphorus Adsorption Capacity with Soil Properties by Depth

The two point P adsorption capacities of *D1* and *D2* had a significant positive linear correlations with Al and SOM irrespective of the initial P concentrations (Table 5.5) and variations of Al and SOM between the two depths (Table 5.3). Al and SOM were determined to be the main contributing factors for higher P adsorption, as also previously reported (Börling et al., 2001; Daly et al., 2015; Moazed et al., 2010; Szafranek & Skłodowski, 1999; Villapando & Graetz, 2001). Furthermore, the point P adsorption capacities of the tested Nfld soils had a significant positive linear correlations with the soil

moisture content, which might be due to a significant correlation of moisture content with SOM (r = 0.51) (Table 5.5).

On the other hand, Fe extracted by Mehlich-3 and P extracted by Mehlich-3, 1% citric acid, and water were negatively correlated with P adsorption capacity irrespective of the initial P concentrations. Remarkably, silt had a significantly negative linear correlation with P adsorption capacity of *D2* soils irrespective of the initial P concentrations (Table 5.5). In agreement with Villapando and Graetz (2001), there was a significant negative correlation between P adsorption and extracted Fe (Table 5.5), which strengthens the argument that the Al oxides and possibly Al-organic chelates play a major role in P adsorption.

The two-point P adsorption capacities were not significantly correlated with clay content or pH (Table 5.5). Previous studies reported both lower P mobility in soils with high clay (do Nascimento et al., 2018), no impact of clays (Börling et al., 2001) or positive correlation of P adsorption parameters with clay content (Moazed et al., 2010). This suggests that mineralogy and metal oxides also have a role beyond the simple textural classification. Furthermore, long-term liming may mask the relation between P adsorption with clay and pH by modifying the clay surface charges. The linear correlations of P adsorption with extractable P, Al, Fe, and SOM suggest that these parameters may be used as input variables in pedotransfer functions to estimate the P adsorption capacity of the tested soils. The pH range was near the ideal range for availability and was likely not wide enough to allow for sufficient impact.

Table 5.5. Pearson linear correlation (p = 0.05) between P adsorption capacity and soil variables for managed SJRDC soils collected from 0-20 or 20-40 cm depths (n=23).

Variables	*Treated with 150 mg P L^{-1}*		*Treated with 500 mg P L^{-1}*	
	0-20 cm	20-40 cm	0-20 cm	20-40 cm
M3-P	**-0.51**	**-0.48**	**-0.51**	**-0.31**
M3-Fe	**-0.53**	**-0.50**	**-0.28**	**-0.60**
M3-Al	**0.61**	**0.59**	**0.32**	**0.51**
M3-Ca	***NS***	***NS***	***NS***	**0.31**
H_2O-SrP	NS	**-0.35**	**-0.30**	NS
CA-SrP	**-0.29**	**-0.29**	**-0.42**	NS
M3-srP	**-0.47**	**-0.46**	**-0.52**	**-0.29**
Clay	NS	NS	NS	NS
Silt	NS	**-0.33**	NS	**-0.27**
Sand	NS	**0.29**	NS	NS
MC	**0.35**	**0.56**	**0.49**	**0.61**
SOM	**0.47**	**0.57**	**0.57**	**0.68**
pH	NS	NS	NS	**0.25**

NS: not significant (p>0.05), M3-P, M3-Fe, M3-Al, and M3-Ca represent phosphorus (P), iron (Fe), Aluminium (Al), and calcium (Ca) measured by ICP-OES in Mehlich-3(M3) extract, respectively. H_2O-SrP, CA-SrP, and M3-SrP represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis.

5.4.4. Pedotransfer Functions for Phosphorus Adsorption Capacity Using Selected Soil Properties

Soil variables identified to have a significant correlation with the point P adsorption capacity, based on a simple linear correlation (Table 5.5) and the PCA correlation matrix (Table S5.2, Supplementary Material) were used as independent variables for a predictive linear multiple regression. Collinear independent variables that were weakly correlated with dependent variables were excluded from the model.

The SOM alone explained about 20-50% of the variability of the P adsorption capacity for both *D1* and *D2* soils (Table 5.6). The negative correlation between SOM and Fe (r = 0.48 and 0.59), and Al and Fe (r = 0.31 and 0.63) for *D1* and *D2* soils demonstrated the dominant

role of SOM and Al in P adsorption (data not presented), an observation supported by other studies (Gustafsson, 2006; Warrinnier et al., 2019). The SOM of *D1* and *D2* soils was greater than for soils in Canadian Atlantic provinces (Benjannet, Khiari, et al., 2018; Benjannet, Nyiraneza, et al., 2018; Nyiraneza et al., 2017), likely due to long-term management or organic matter supplied from long-term manure application (Maillard & Angers, 2014).

Another important P adsorption predictor was the Al content of the soil, which explained up to 37% of the P adsorption variability, and better predictor in *D1* soils (Table 5.6). Villapando and Graetz (2001) concluded that copper chloride-extracted Al (organic matter-bound Al) was the major single factor controlling over 60% of the variability in P adsorption by the Bh horizon of Podzols (Villapando & Graetz, 2001).

The total P extracted by Mehlich-3 explained ~26% of the variability in the P adsorption capacity when the soils treated with lower initial concentration (Table 5.6). The long-term fertilized soils expected to decrease the soil's P adsorption capacity (Bhattacharyya et al., 2015) but the tested soils had not reached it's P adsorption capacity. The presented models can be used to predict the P adsorption index of the long-term managed fields from routine soil tests in similar settings. However, the use of the P adsorption capacity or soil test P for environmental risk assessments must be verified by field studies (Buczko & Kuchenbuch, 2007; Djodjic et al., 2004).

Table 5.6. Stepwise multivariate regression results for the relationships between P sorption parameters and selected soil variables. Only the variable with R^2>0.05 are presented. R^2 is the coefficient of determination or proportion of variance explained by the model.

Dependent Variable[£]	*Independent Variable*	*Coefficient*	*Standard Error*	*p-value*	*Partial R^2*
q1	Constant	1.16	0.039	<0.001	
	M3-P	-2.00×10^{-3}	0.27×10^{-3}	0.267	0.26
	M3-Fe	-0.89×10^{-4}	0.79×10^{-4}	<0.001	0.28
	M3-Al	1.13×10^{-4}	1.94×10^{-5}	<0.001	0.37
	CA-P	4.16×10^{-4}	7.78×10^{-5}	<0.001	0.08
	SOM	5.72×10^{-3}	1.25×10^{-3}	0.110	0.22
q2	Constant	4.63×10^{-1}	1.24×10^{-1}	<0.001	
	M3-Fe	6.13×10^{-4}	1.59×10^{-4}	<0.001	0.25
	M3-Al	2.20×10^{-4}	2.88×10^{-5}	<0.001	0.35
	CA-P	-2.89×10^{-4}	4.96×10^{-5}	<0.001	0.08
	Silt	-2.74×10^{-3}	9.75×10^{-4}	0.007	0.11
	SOM	2.05×10^{-2}	2.79×10^{-3}	<0.001	0.32
	pH	5.82×10^{-2}	1.22×10^{-2}	<0.001	0.03
q3	Constant	-3.68	1.63	0.027	
	M3-P	3.02×10^{-2}	1.76×10^{-2}	<0.001	0.26
	M3-Fe	2.42×10^{-3}	1.15×10^{-3}	0.039	0.08
	M3-Al	1.29×10^{-3}	4.08×10^{-4}	0.002	0.10
	H_2O-P	2.96×10^{-1}	2.60×10^{-1}	0.260	0.07
	CA-P	4.98×10^{-3}	2.31×10^{-3}	0.035	0.17
	M3-srP	-5.25×10^{-2}	2.41×10^{-2}	0.033	0.28
	SOM	6.08×10^{-2}	2.55×10^{-2}	0.020	0.32
q4	Constant	-5.54	9.54×10^{-1}	<0.001	
	M3-P	-6.73×10^{-2}	2.76×10^{-2}	0.018	0.10
	M3-Al	1.82×10^{-3}	2.27×10^{-4}	<0.001	0.26
	CA-P	-3.05×10^{-3}	1.08×10^{-3}	0.006	0.03
	M3-srP	7.05×10^{-2}	2.82×10^{-2}	0.015	0.09
	SOM	1.51×10^{-1}	1.67E-02	<0.001	0.47
	pH	6.62×10^{-1}	1.13×10^{-1}	<0.001	0.06

[£]q1 and q2 represent the P adsorption capacity of *D1* (0-20 cm) soils treated with 150 and 500 mg P L^{-1} initial concentrations, and q3 and q4 represent the P adsorption capacity of *D2* (20-40 cm) soils treated with 150 and 500 mg P L^{-1} initial concentrations, respectively.

5.5. Conclusions

This study measured for the first time the status of P adsorption capacity in long-term managed (~150-160 years) agricultural podzolic soils in Eastern Nfld and soil properties influencing the P adsorption capacity of the soils. The long-term managed 0-20 cm soil layer had higher legacy P, SOM, EC, K, and Fe than the 20-40cm soils. The reverse applied for Al. The P accumulation in the topsoils and potential vertical P mobility to the subsurface soil layers signals the need for proper management of P in such soils. The tested topsoil likely acts as both source and sink for P while the subsurface layer acts as a P sink.

The effect of long-term liming was reflected in the pH of both soil layers. The measured P adsorption capacities were comparable for both soil layers at the low P concentration solution; however, the solution with higher P concentration indicated to a higher P adsorption capacity in the subsurface soil, a phenomenon attributable to higher Al content. Therefore, a higher initial P concentration of 500 mg P L^{-1} is recommended for assessing the single-point P adsorption capacity of similar Podzols. Soil organic matter, Al, and total P may be employed to predict P adsorption capacity and thus employed to develop testable hypotheses for the development of environmentally and economically viable P management strategies for acidic soils in boreal regions.

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5.7. Supplementary Material

Table S5.1. The phosphorus adsorption capacity of soil collected at 0-20 cm (D1) and 20-40 cm (D2) depths from 23 managed SJRDC fields treated with 150 and 500 mg $P L^{-1}$ initial concentrations. The values in the table are presented as mean and standard error (SE) calculated from triplicated sample size (n = 3). Results reported as mg $P g^{-1}$ of dry soil.

Field	*Treated with 150 mg P L^{-1}*		*Treated with 500 mg P L^{-1}*	
	0-20 cm (*D1*)	20-40 cm (*D2*)	0-20 cm (*D1*)	20-40 cm (*D2*)
	Mean (SE)	Mean (SE)	Mean (SE)	Mean (SE)
F1	1.37(0.005)	1.41(0.006)	2.64(0.082)	3.15(0.130
F2	1.40(0.001)	1.42(0.015)	2.87(0.064)	2.93(0.061)
F3	1.35(0.006)	1.33(0.009)	2.57(0.032)	2.76(0.022)
F4	1.37(0.004)	1.39(0.012)	2.86(0.075)	2.99(0.090)
F5	1.32(0.006)	1.32(0.006)	2.33(0.067)	2.80(0.170)
F6	1.34(0.002)	1.36(0.004)	1.97(0.039)	2.87(0.094)
F7	1.30(0.002)	1.28(0.006)	1.66(0.037)	2.51(0.080)
F8	1.33(0.000)	1.32(0.002)	1.66(0.210)	2.46(0.028)
F9	1.39(0.002)	1.38(0.007)	2.65(0.173)	2.75(0.040)
F10	1.33(0.001)	1.28(0.002)	1.83(0.018)	2.26(0.180)
F11	1.36(0.004)	1.34(0.008)	2.51(0.075)	2.79(0.135)
F12	1.33(0.004)	1.32(0.002)	2.09(0.039)	2.74(0.135)
F13	1.32(0.004)	1.29(0.003)	1.81(0.144)	2.38(0.170)
F14	1.39(0.009)	1.41(0.006)	2.50(0.093)	3.11(0.111)
F15	1.35(0.007)	1.27(0.010)	2.32(0.044)	2.08(0.006)
F16	1.33(0.006)	1.33(0.004)	1.86(0.082)	2.79(0.054
F17	1.41(0.001)	1.34(0.010)	2.68(0.241)	2.56(0.057)
F18	1.30(0.001)	1.25(0.009)	1.98(0.096)	2.01(0.091)
F19	1.30(0.006)	1.23(0.005)	2.04(0.224)	1.90(0.159)
F20	1.41(0.001)	1.36(0.011)	2.97(0.041)	2.89(0.059)
F21	1.36(0.019)	1.29(0.006)	2.27(0.061)	2.09(0.084)
F22	1.30(0.001)	1.27(0.002)	1.86(0.059)	1.98(0.057)
F23	1.20(0.004)	1.16(0.001)	1.80(0.078)	0.58(0.070)
Range	1.20-1.41	1.66-2.97	1.16-1.42	0.46-3.38
Mean (SE)	1.34(0.010)	1.32(0.013)	2.25(0.087)	2.50(0.117)
Median	1.34	1.32	2.27	2.74

Table S5.2. Principal components (PC) and component loadings (correlation matrix) for soil physicochemical variables and P adsorption capacity (n=46, representing D1 and D2 soils); bold component loading values were used to interpret the PCs.

Variables	*Principal Components*			
	PC 1	PC 2	PC 3	PC 4
M3-Ca	**0.721**	0.497	0.106	-0.415
M3-K	**0.835**	0.044	0.280	0.002
M3-P	**0.778**	-0.451	0.359	0.101
M3-Fe	0.526	-0.195	**-0.609**	0.051
M3-Al	**-0.727**	-0.060	0.430	0.409
H_2O-SrP	**0.851**	0.012	0.173	0.136
CA-SrP	**0.600**	-0.491	0.500	0.047
M3-SrP	**0.757**	-0.479	0.380	0.078
PAC-150	-0.240	**0.720**	0.436	0.182
PAC-500	-0.460	**0.648**	0.385	0.038
Clay	**0.487**	0.281	-0.094	0.475
Silt	**0.601**	0.357	**-0.601**	0.250
Sand	**-0.646**	-0.381	0.525	-0.352
SOM	0.361	**0.635**	0.371	0.229
pH	0.248	0.311	-0.047	**-0.821**
EC	**0.755**	0.305	0.283	-0.188
Eigenvalue	6.33	2.848	2.402	1.587
%variance	39.57	17.80	15.01	9.919

Soil organic matters (SOM), electrical conductivity (EC); *H_2O-SrP, CA-SrP, and M3-SrP represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis;* M3-Ca, M3-K, M3-P, M3-Fe, and M3-Al are calcium (Ca), potassium (K), phosphorus (P), iron (Fe), and aluminium (Al) analysed by ICP-OES in Mehlich-3 (M3) extract, below the detection limit (BDL) of 0.01 mg P kg^{-1} which varies for the different tests. PAC-150 and PAC-500 represented a P adsorption capacity of soils treated with 150 mg P L^{-1} and 500 mg P L^{-1}, respectively.

Chapter 6. AVAILABILITY AND UPTAKE OF PHOSPHORUS FROM PODZOLS AMENDED WITH DISTINCT TYPES OF P SOURCES AND BIOCHAR

6.1. Abstract

Phosphorus (P) availability and uptake depend on the soil's buffering capacity as related to pH, soil organic matter (SOM), and P sink and sources. In Podzols, especially when newly converted from forested state to agricultural use, the size of the P sinks, fluxes, and thus the soil's P buffering capacities can vary with depth and variable soil chemistry. Therefore, this study aimed to investigate the P availability and uptake and their inter-relationship in recently converted Podzols. A fully-replicated (5 randomized blocks) greenhouse pot experiment was carried out to assess the effect of newly converted Podzols (collected from a depth of 0-15 cm or 15-30 cm or soil A and B) and different P sources (mineral fertiliser, dairy manure, fractions of recirculating aquaculture system (RAS) slurry, and supernatant) on P availability and its uptake by tall fescue (*Festuca arundinacea*), both in the shoot and in the root biomass. The impact of biochar on P availability and uptake was also tested for the topsoil layer. The experiment was carried out over 12 weeks, with soils maintained at field capacity for water. The relationship between the availability of P as determined by soil P-*tests* and the uptake of P by plants was evaluated in the context of a series of soil parameters, as measured at the end of the experiment. Soil A treated with dairy manure, RAS slurry, and biochar had increased pH and SOM. The Olsen method extracted significantly higher P in soil A than soil B while the reverse was true for Mehlich-3

($p<0.05$). In contrast citric acid extracted significantly higher P in soil A treated with RAS slurry compared to Olsen and Mehlich-3 methods. Moreover, less than 0.50 mg P kg^{-1} was extracted by deionized water, which indicates strong P adsorption. Furthermore, better linear correlations and regressions were observed between P availability extracted by P-*tests* and uptake, dry mass shoot yield for soil A than soil B treatments. Thus, the P availability and uptake in recently converted Podzols depends on the P sources, soil depth, and SOM.

Key words: phosphorus availability, phosphorus sources, phosphorus uptake, Podzols

6.2. Introduction

Phosphorus (P) is a vital element for plants' cellular growth and division, energy storage, photosynthesis, respiration, and other metabolic processes (Margalef et al., 2017; Mullins, 2009; Schachtman et al., 1998). Also, it is the second most limiting nutrient in crop production (Elser, 2012). The applied inorganic or organic P sources must transform into readily available P in the form of $H_2PO_4^-$ and HPO_4^{2-} based on the soil pH (Reid et al., 1987). The monovalent orthophosphate ($H_2PO_4^-$) is the most easily absorbed readily available P species by plant roots from the soil solution (White, 2008). Some mineral P fertilisers are easily soluble in the soil, while some granular fertilisers are gradually soluble (do Nascimento et al., 2018; Khatiwada et al., 2012). In contrast the organic P input from organic fertiliser or the legacy organic P, which comprises about 20-80% of the soil P pool (Dalal, 1977), must transform to orthophosphate before plant uptake (Bünemann, 2015; Huang et al., 2017). The availability of P in the soil solution or available for plant uptake depends on the soil adsorption or buffering capacity, soil pH, soil organic matter (SOM), cation exchange capacity, rhizosphere microbiomes, root length and density, fertiliser type, tillage, and environmental factors (Fageria & Moreira, 2011; White, 2008; Ziadi et al., 2013). Soil pH has a significant influence on the availability of P in the soil solution, i.e., at pH<7.2 monovalent orthophosphates ($H_2PO_4^-$) are the dominant species while above 7.2 divalent orthophosphate (HPO_4^{2-}) are the dominant available P species (Ziadi et al., 2013). Also, aluminium (Al), iron (Fe), and SOM in acid Podzols common in Newfoundland and Labrador (NL) and elsewhere fix the available P species on the surface of clay minerals or organometallic materials (Grand & Lavkulich, 2015) (also discussed in Chapters 4 and 5).

SOM-bound P might easily mineralize while the P fixed on the mineral surface depends on the strength and complexation of the compound. Studies have suggested that amending the infertile soils with organic materials like biochar, manures, fish waste, and plant residues helps to improve soil properties and serve as P activators (Abedin, 2015; Kumaragamage et al., 2011; López-Mosquera et al., 2011; Qian et al., 2004; Yang et al., 2019; Zheng et al., 2019; Zhu et al., 2018). For example, the recirculating aquaculture system (RAS) wastes are rich in nutrients and SOM can function as fertiliser and organic carbon amendments in poor soil (Bregnballe, 2015; Danner et al., 2019; Van Rijn, 2013). Similarly, biochar is used to improve soil properties like pH, SOM and P availability (Abedin, 2018; Ding et al., 2016; Glaser & Lehr, 2019; Han Weng et al., 2017; Martinsen et al., 2014; Solaiman et al., 2019; Zhu et al., 2018). A meta-analysis by Glaser and Lehr (2019) reported a significant increase in P availability in agricultural soils amended with biochar (Glaser & Lehr, 2019). Thus, it is important to understand the impact of newly converted Podzolic soils on P availability as a function of different P sources and organic carbon amendments and the uptake of available P by the plant.

In this study, tall fescue (*Festuca arundinacea*) (Hand et al., 2010) was used to assess P uptake in newly converted Podzolic soils treated with different P fertilisers and biochar. Tall fescue was chosen because it is the most common forage and pasture grass in wet regions, including southern parts of Canada, British Columbia, Alberta, Ontario, and Nova Scotia's west coast (Beef Cattle Research Council, 2013). Also, it is the most productive and fast-growing grass species suitable for wet and acidic soils (Dane et al., 2006; Drapeau et al., 2007; Singer et al., 2003).

The available P has been quantified with several P-*tests* proposed for specific soil types and properties for different purposes in different regions (Buondonno et al., 1992; Harmsen, 2007; Kleinman et al., 2001; Morgan & Mahmoud, 2016; Nawara et al., 2017; Peck, 1990; Watson & Mullen, 2007; Wuenscher et al., 2015). The P-*test* selection criteria mainly depend on the soil pH and relationship with plant response. However, Mehlich-3 is the standard method currently used in NL to measure P availability for fertiliser recommendations; Mehlich-3 based recommendations have not been yet fully calibrated for NL soils and crop responses. Furthermore, the universality of a P-*test* for extracting available P from both long-term agricultural fields and in newly converted forest Podzols has not been scrutinised. Citric acid extracted significantly more soil P than other P-*tests,* including Mehlich-3 for NL soils (Chapter 3). Nevertheless, Mehlich-3-P was strongly correlated with Bray-1-P, Mehlich-1-P, Bray-2-P, Olsen-P and citric acid-P (Chapter 3). Even though strong correlations were previously reported between Mehlich-3-P and plant P uptake (Ziadi et al., 2001), there is a lack of understanding of the relation between P-tests and plant responses in the recently converted from boreal forest and long-term established NL Podzols.

It was hypothesized that the relationship between P-*test* estimates and plant uptake varies with soil layer (i.e., 0-15 cm and 15-30 cm), and that, consequently, the availability of P from the various types of fertiliser varies between the two soil layers. The layers have been selected to represent soils depths that are brought to the surface and variably mixed during land-use conversion from forest to agricultural use.

Therefore, this study aimed to (1) investigate the P availability and uptake (extractability) in a scenario that is relevant to Podzols recently converted from natural state to agricultural

use (0-15 cm and 15-30 cm) (2) assess the role of the P source form P availability to tall fescue in a greenhouse pot experiment, and (3) evaluate a regression relationship between the P availability (as tested with citric acid, Olsen, Mehlich-3, and water methods) and P uptake in both root and shoot biomass, and shoot dry mass of tall fescue.

6.3. Materials and Methods

6.3.1. Site Description, Soil Types, P Sources, and Biochar Use

Composite soil samples were collected in June 2018 from a forested field cleared in August 2017. The field is located at the Center for Agriculture and Forestry Development (CAFD), in central Newfoundland (Nfld). The site description was provided in Chapter 4. This field was under forestry management and was mainly planted with orchard trees. The field has a history of receiving inconsistent rates of mineral fertilisers (34-0-0, 10-10-10, 0-0-49, and 18-09-18) between the 1990s and 2017, when the field converted to agriculture use; there is no history of manure use (B. Linehan, personal communication). Ferrohumic Podzol is the dominant soil type in the area (east of Grand Falls-Windsor) (Amor, 2010).

Representative soil samples were collected from 3 locations at a depth of 0-15 cm (henceforth called soil A) and 15-30 cm (henceforth called soil B) using a backhoe. The triplicate samples were homogenized for each soil type and air-dried in the greenhouse conditions. The soils were passed through 4 mm sieve to remove coarse materials for the pot experiment.

Four P sources: (1) mineral fertiliser, (2) dairy manure, (3) RAS slurry and (4) RAS supernatant were used to supply 110 kg P ha^{-1} and 200 kg N ha^{-1} for the tall fescue in the

pot experiment. The RAS waste was collected from a fish farm located on the western shore of Nfld (Northern Harvest Smolt, Ltd.). Dairy manure was collected from the open lagoon of a dairy farm located in the Cormack NL area in June 2018. The RAS waste and dairy manure were stored at 4°C until the application time. Before application, the RAS waste and dairy manure were agitated and stabilized in the greenhouse environment. A single rate (40 t ha^{-1}) of wood-based biochar was applied to soil A in combination with different P sources aimed to supply equivalent amounts of P. The biochar rate was selected in accordance to previous research on similar soils in Labrador (Abedin and Unc, 2020). In contrast, soil B was only treated with P sources.

6.3.2. Initial Characterization of Soil, Dairy Manure, RAS Waste, and Biochar

The summary of protocols used to analyze selected soil, biochar, dairy manure and RAS waste are available in Table 6. 1. The baseline characterisation of fertiliser materials and soils are presented in Table 6. 2 and Table 6. 3, respectively. Both soil A and B were acidic soils with a pH of 5.3, as measured in saturated paste (Carter & Gregorich, 2008). Soil A had slightly more soil organic carbon (SOC) than soil B. On the other hand, soil A had about 12-fold more ammonium-nitrogen (NH_4-N) and 2-fold more nitrate-nitrogen (NO_3-N) than soil B. Also, soil A has higher available P (colorimetrically measured in Olsen and citric acid extracts) than soil B, but the Mehlich-3 extractable P was slightly higher in Soil B than A (Table 6. 3). In contrast, the total citric acid P, measured using ICP-OES, was higher in soil A than B similar to colorimetric analysis of available P in Olsen and citric acid extracts.

Soil A had a higher level of Al and Fe than soil B for both citric acid and Mehlich-3 extracts (Table 6. 3). This could be related to the soil texture: soil A might have retained these minerals in the amorphous form in contrast to soil B, which might have a stable minerals, though the mineral species were not measured in this study. Soils A and B used in this study share similar soil properties with the *unmanaged* 0-15 and 15-30 cm soils of Labrador used for the pilot experiment (Abedin, 2018), *unmanaged* SJRDC horizons, and *unmanaged* CAFD horizons (Chapter 4). Higher Al content was measured in soil A and B compared to the Prince Edward Island (PEI) soil while Fe was higher in the PEI soils (Benjannet et al., 2018). This underscores the regional soil variability and the importance of knowing the soil's mineral composition of a specific region to better understand their interaction with the nutrients and to inform the selection of a proper P-*test*.

Table 6. 2 shows the initial nutrient composition of biochar, dairy manure, RAS slurry, and supernatant. Wet samples of dairy manure, RAS slurry, and supernatant have a composition of 0.02%, 1.66%, and 0.001% P, respectively. The RAS slurry was rich in N and P content compared to the dairy manure and RAS supernatant, similar to previous reports (Chen et al., 1997; Yeo et al., 2004). The biochar, dairy manure, and RAS slurry have organic carbon compositions of 75.1%, 29.6%, and 26.3%, respectively, based on dry matter (Table 6. 2). Potassium (K) and carbon (C) were not detected in the RAS supernatant (Table 6. 2). The biochar used in this study has 320 mg P $kg^{-1,}$ while about 700 mg P kg^{-1} was reported in another biochar by Abedin (2018). This could be due to the differences in feedstock and production processes (Ding et al., 2016; Spokas et al., 2012).

The field water holding capacity of 0.175 L of water per L of soil was estimated using Sexton method (Saxton & Rawls, 2006) based on the measured bulk density of 1.2 kg L^{-1} for both soil A and B.

Table 6. 1. Summary of soil tests used for soil, plant tissue, dairy manure, and RAS waste analysis.

Test	Sample	Method (Carter & Gregorich, 2008; OMAFRA, 2009)
pH	Dry soil	saturated paste 1:1 soil to water
Carbon package (IC, OC, and TC), % dry	Dry soil	Combustion method, Vario Macro cube CHNS analyser
Total nitrogen, % dry	Dry soil, plant	Combustion method, CHNS analyser
NH_4-N, mg kg^{-1} (wet)	tissue, $dairy	KCl extractable
NO_3-N, mg kg^{-1}	manure and $RAS	KCl extractable
Mg, Ca, Na and K, mg kg^{-1}	waste	1N ammonium acetate extractable, ICP-OES
Available soil P, mg kg^{-1}		Olsen*, 1% citric acid, water and Mehlich-3, spectrophotometry
Total soil P, mg kg^{-1}		1% citric acid and Mehlich-3, ICP-OES
Multiple nutrients, mg kg^{-1}	Dry soil	1% citric acid and Mehlich-3, ICP-OES
Dry matter, %	Diary manure and RAS	Oven dry at 105 ºC
P, K, Ca, and Mg, % dry	plant tissue	Microwave/acid digestion, ICP-OES
Micronutrients, mg kg^{-1}	plant tissue	Microwave/acid digestion, ICP-OES

*Available soil P in the Olsen extract analyzed by colorimetric using Seal AA3 spectrophotometer. $The concentration of N, P, K in dairy manure and RAS waste were reported on the wet mass.

Table 6. 2. Baseline characteristics of RAS waste, dairy manure, and biochar.

Materials	DM	K	TKN	†*P*	*TC*	*IC*	*OC*	*NH_4-N*	*NO_3-N*
	----------%----------							-----mg kg^{-1}----	
Dairy Manure	1.79	0.16	0.13	0.02	34.6	5.0	29.6	858	3.58
Slurry	17.7	0.007	1.11	1.66	27.2	0.93	26.30	2350	1.46
Supernatant	0.05	#ND	0.008	0.001	*NA	NA	NA	211	0.74
Biochar	NA	NA	NA	320	75.4	0.33	75.10	NA	NA

**Not analyzed (NA), #not detected (ND),* †P in biochar expressed as mg kg^{-1} in dry mass, dry matter (DM); K, total Kjeldhal nitrogen (TKN), P, NH_4-N, and NO_3-N were determined in wet sample.

Table 6. 3. Baseline characteristics of soil A and B used for the pot experiment.

Methods	Soil Properties	Soil A	Soil B
1:1 soil/water	pH	5.3	5.3
Combustion	Total Carbon, % dry	0.96	0.85
	Inorganic Carbon, % dry	0.02	0.02
	Organic Carbon, % dry	0.93	0.83
KCl extraction	NH_4-N, mg kg^{-1}	36.5	3.31
	NO_3-N, mg kg^{-1}	6.26	3.59
Citric acid (Colorimetric)	Available P, mg P kg^{-1}	20.72	9.75
Olsen (colorimetric)	Available P, mg P kg^{-1}	25	20
Ammonium acetate	Magnesium, mg Mg kg^{-1}	14	7.9
	Potassium, mg K kg^{-1}	110	80
Mehlich-3(ICP)	Calcium, mg Ca kg^{-1}	29.5	21.6
	Magnesium, mg Mg kg^{-1}	5.3	3.6
	Potassium, mg K kg^{-1}	54.5	46.9
	Phosphorus, mg P kg^{-1}	36.5	41.4
	Iron, mg Fe kg^{-1}	73	46.4
	Copper, mg Cu kg^{-1}	0.4	0.4
	Manganese, mg Mn kg^{-1}	9.1	9.8
	Zinc, mg Zn kg^{-1}	1.4	0.8
	Boron, mg B kg^{-1}	0	0
	Sodium, mg Na kg^{-1}	4.3	3.1
	Aluminium, mg Al kg^{-1}	1775.9	1692.7
	Sulphur, mg S kg^{-1}	15.9	7.7
Citric acid (ICP)	Calcium, mg Ca kg^{-1}	56.35	42.5
	Magnesium, mg Mg kg^{-1}	9.21	7.07
	Potassium, mg K kg^{-1}	74.08	61.86
	Phosphorus, mg P kg^{-1}	21.96	6.91
	Iron, mg Fe kg^{-1}	192.08	97
	Copper, mg Cu kg^{-1}	0.37	0.29
	Manganese, mg Mn kg^{-1}	48.86	42.51
	Zinc, mg Zn kg^{-1}	1.54	0.32
	Boron, mg B kg^{-1}	0.68	0.4
	Sodium, mg Na kg^{-1}	8.4	6.82
	Aluminium, mg Al kg^{-1}	1573.79	921.51
	Sulphur, mg S kg^{-1}	11.64	12.86

6.3.3. Experimental Design

The experiment comprises a total of 14 treatments representing soils A and B, fertilisers, and biochar amendments. The control treatments were soils A and B without fertiliser or

biochar, while for the other treatments; the soils received a fixed amount of 110 kg P ha^{-1} and 200 kg N ha^{-1} based on the initial P content in the soil and biochar. The control soils only received water to maintain them at field capacity.

The soil, fertiliser, biochar, and water were manually homogenized in one clean tote per treatment similar to Sikora et al. (1982) (Sikora et al., 1982). About 3.45 kg of treated and control soils were potted in each of 5 pots (replicates) seeded with 1.0 g tall fescue seeds (*Festuca arundinacea*, cultivar variety of kokanee); seeds were manually dispersed on the surface. Pots were randomly assigned to five rows, each considered a block, on a bench in the greenhouse.

The experiment was conducted over 12 weeks from August-November 2018 in the CAFD tree nursery greenhouse. Every few days, two pots per block were randomly selected to monitor water loss to keep pots at field capacity. The agronomic data such as time to germinate, leaf stages, leaf width, plant heights and plant vigour rating was recorded weekly while chlorophyll reading was collected on a biweekly basis.

6.3.4. Post-harvest Soil and Biomass Analysis

Before the flowering stage, the above-ground biomass (shoots) and the root biomass were harvested. Additionally, the soil of each treatment (pot) was retrieved for further analysis. The wet roots and shoots were dried at 60 °C for 48 h and milled for further analysis. Similarly, the soil was air-dried for 3 to 5 d in a temperature-controlled room (~35 °C with air movement) and then passed through a 2 mm size sieve. The nutrient concentration in the soil and root and shoot biomass of tall fescue were measured using the methods summarized in Table 6. 1. The air-dried roots and shoots of tall fescue were milled, and the

powder was sent to the Agriculture and Food Laboratory at the University of Guelph for nutrient analysis along with the soil samples.

Additionally, the soil P was extracted with water, citric acid and Mehlich-3 methods and analysed with colorimetric and ICP-OES methods (details presented in Chapter 3) in addition to the Olsen method used by the Agriculture and Food Laboratory of the University of Guelph. The summary of soil and plant tissue extraction methods and analysis techniques used in this study are presented in Table 6. 1. Furthermore, the P uptake was calculated by multiplying P concentration (% dry) with dry mass root or shoot biomass per pot. The yield of the dry shoot biomass was reported in mega gram per hectare (Mg ha^{-1}).

6.3.5. Statistical Analysis

The descriptive and explanatory statistical analysis was performed using IBM SPSS version 25 (SPSS Inc, 2017), PAST3 (Hammer et al., 2001), and Origin Lab 2020 ("Origin(Pro), Version 2019b. OriginLab Corporation, Northampton, MA, USA.," 2019) programs. The test for normality was evaluated using the Shapiro-Wilk test (Ghasemi & Zahediasl, 2012; Uyanık & Güler, 2013). A one-way analysis of variance (ANOVA) was performed using a general linear model for the important response parameters by using treatment as a fixed factor. Post-hoc Tukey's pairwise comparisons were applied to compare the mean of measured parameters in the soils or plants as a factor of treatments. Also, linear correlation (Pearson, r) and regression coefficient of determination (R^2) were assessed between selected soil and plant parameters. A significance level of 0.05 was used for all statistical tests.

6.4. Results and Discussion

6.4.1. Effects of Biochar and P Sources on Selected Soil Properties

The pH of soils A and B treated with dairy manure significantly increased from 5.3 (initial pH) to almost 6.0 (post-harvest) regardless of the biochar amendment (Table 6. 4). A similar trend was reported in other studies (Achat et al., 2014; Dale et al., 2015; Whalen et al., 2000). This could be related to the buffering property of the dairy manure. Similarly, acidic soils in Alberta treated with dairy manure for eight weeks in the laboratory showed increased soil pH due to the buffering effects of bicarbonates and organic acids (Whalen et al., 2000). Also, soil A treated with mineral fertiliser and RAS supernatant and amended with biochar had a significant increase in soil pH compared to the same treatment without biochar amendment but not significantly different than control treatments. This may be related to the acid-neutralizing or liming effects of the biochar (Glaser & Lehr, 2019).

On the other hand, the biochar amendment did not affect the pH of soil A treated with dairy manure or RAS slurry (Table 6. 4). This implies the biochar in combination with organic fertilisers rich in SOM has a limited effect on soil pH, which might be masked by SOM effects. However, a significantly lower pH was observed in soils treated with mineral fertilisers compared to the control treatments which could be related to the nitrogen mineralization effect. Another greenhouse study reported that the soil treated with 300 mg P kg-1 mineral fertiliser and planted with tall fescue had increased soil pH (Paredes et al., 2011). Thus, the effects of biochar might be fertiliser dependent. Overall, in agreement with Abedin (2018), soil A amended with biochar had an increased soil pH ($p = 0.04$). Soils treated with dairy manure had a similarly increased pH ($p<0.05$) as compared to other

fertilizers. Also, other studies (Abedin, 2018; Glaser & Lehr, 2019; Han Weng et al., 2017; Latawiec et al., 2019; Solaiman et al., 2019; Zheng et al., 2019) reported a similar effect of biochar on the soil pH under various treatment conditions, as most of the biochar studied has an alkaline pH, which has a liming effect on the acid soils (Glaser & Lehr, 2019). On the other hand, soil pH was negatively correlated with P uptake by tall fescue shoots (r = 0.38), yield of shoot dry mass (r = 0.50) and available and total P in the post-harvested soil A treatments amended with biochar, while soil pH was positively correlated (r= 0.42) with water-extractable P (Table 6. 8). This could be explained by the effect of biochar on P adsorption.

The other important soil quality indicator expected to improve with the biochar or organic fertiliser amendment was SOC. About a 3-fold increase of SOC was observed in soil A that received biochar compared to no biochar (Table 6. 4). The SOC in soil A treated with mineral fertiliser, RAS slurry or supernatant without biochar was not significantly different between these treatments compared to the soil A control treatment. Similarly, the SOC in soil B was not affected by the type of P source compared to soil B control (Table 6. 4). This could be related to the loss of easily degradable or unstable carbon in the dairy and RAS waste while the forms of carbon in the biochar are relatively stable (Han Weng et al., 2017). Biochar significantly increased the SOC in soil A in agreement with several other studies conducted under different conditions (Abedin, 2018; Glaser & Lehr, 2019; Latawiec et al., 2019; Solaiman et al., 2019; Zheng et al., 2019). Overall, as witnessed from the significant positive correlation between SOC and tall fescue responses (P uptake, yield, and chlorophyll) in this study, biochar is a good candidate to improve soil fertility parameters like pH and SOM (Mia et al., 2014; Zheng et al., 2019). Furthermore, the NO_3-N, Ca, and

Fe in the soil A treatments amended with biochar has a significant positive correlation with tall fescue responses.

6.4.2. Effects of Soil Types, Biochar, and P Sources on P Extractability

The P (both available and total) in soils A and B before and after the experiment was quantified. Table 6. 3 shows that the Olsen and citric acid methods extracted relatively more available and total P from the unamended soil A than soil B (i.e., before the soils were treated with different P sources and biochar amendment) while the reverse trend was observed for Mehlich-3. This could be explained by the differences in mineral content responsible for fixing P (P species) in soils A and B. Overall, quantitatively, Mehlich-3 extracted more P from both soils compared to the citric acid and Olsen methods, which might suggest that the former method might not reflect the maximum P availability.

On the other hand, Olsen and Mehlich-3 might overestimate the P in mineral soils (Recena et al., 2015). Both the Olsen and Mehlich-3 methods extracted higher P compared to citric acid (Table 6. 3). The higher P extractability in soil A by Olsen and Mehlich-3 might be due to the relatively higher content of amorphous P-fixing minerals like Al, Fe, and organic carbon (Table 6. 3).

Following tall fescue harvest, the residual soil P was extracted by water, Olsen, citric acid, and Mehlich-3 methods. Available (molybdate reactive) and total P in the extracts were measured with colorimetric analysis and ICP-OES, respectively; the means comparison is presented in Table 6. 5. The water-extractable available P (water-aP) was not affected by soil types, biochar, or P sources (Table 6. 5). The lower water-aP in both soils A and B could be related to the higher P adsorption capacity of the podzolic soils as discussed in

Chapter 4, and a negative correlation ($r \approx 0.40$, not significant) was observed between water-aP and Al in soil A (Table S6. 2). In acidic Podzols, excessive mineral Al and organic bound Al are major factors responsible for fixing available P (Cade-Menun et al., 2000; Grand & Lavkulich, 2015b; Villapando & Graetz, 2001), in which deionized water can only extract freely available P, which is affected by soil drying and wetting processes (Ziadi et al., 2013).

However, excessive or repeated P application might overcome the soil's buffering capacity and result in P loss (Kashem et al., 2003; Kumaragamage et al., 2011). In this study, the water-aP was increased by ≈40% in soil A treated with dairy manure and RAS slurry and amended with biochar compared to the control, which implies farms receiving uncontrolled rate of dairy manure have to be monitored and regulated to protect the aquatic environment. The water-aP has been used as an environmental indicator for P loss from the agriculture fields (Khiari et al., 2000; Maguire & Sims, 2002). Hence, the newly converted CAFD Podzols treated with 110 kg P ha^{-1} from different sources did not show a risk of P loss to the environment as they had a 10-20 fold lower water-extractable P than the recommended critical environmental threshold of 9.7 mg P kg^{-1} (Benjannet et al., 2018; Pellerin et al., 2006).

Similarly, available P extracted by Olsen (Olsen-aP) in soil A was not significantly affected by the P sources or biochar, but RAS slurry treatment resulted in significantly higher Olsen-aP (Table 6. 5). The higher Olsen-aP might be related to the easily degradable organic P in the RAS slurry. Even though the biochar did not affect Olsen-aP in soil A (Table 6. 5), but it did affect the correlation between Olsen-aP and Al and improved the correlation with Fe and SOC (Table S6. 3). On the other hand, Olsen extracted significantly lower available P

in soil B regardless of the fertiliser type (P sources) in line with the baseline P trend whereas soil B treated with mineral fertiliser and RAS supernatant (supplemented with mineral P) had significantly higher Olsen-aP than soil B control and soil B treated with dairy manure or RAS slurry. An organic fertiliser might have helped the roots rhizosphere to mineralize, assimilate or uptake more P than soil B treated with inorganic fertilisers. Additionally, the formation of organometallic complexes might serve as a sink for P (Grand & Lavkulich, 2015). Even if Olsen is able to extract P fixed on a mineral and organic soils (Bair, 2012; Tan, 2005), the newly converted CAFD soil B has a strong P-fixing capacity as observed from its significant negative correlation with Al concentration, which implies deep plough should be minimized to reduce excessive P fertiliser recommendation based on the Olsen P-*test*. Also, soil B might help in mitigating P losses (Andersson et al., 2015), but the soil texture and environmental factors might affect its P retention capacity.

Furthermore, citric acid extractable available P (citric-aP) from soils A and B soils has a similar trend with Olsen-aP except for soil A treated with RAS slurry which has significantly higher citric-aP compared to both soil A control and soil A treated with other P sources regardless of biochar amendment (Table 6. 5). Exceptionally, soil A treated with RAS slurry and biochar had significantly higher citric-aP than soil A treated with RAS slurry without biochar amendment (Table 6. 5). This confirmed that the citric acid method is able to extract more soil available P by accounting for organic P in soils with higher SOM than is possible using the Mehlich-3 or Olsen methods; this agrees with the finding in Chapter 3. It was reported that the citric acid solution is able to extract about 80% more hydrolysable organic P than the Olsen solution (Darch et al., 2016; Hayes et al., 2000). Also, soil microbes might play a significant role in mineralizing organic P in RAS slurry,

and additionally, roots exudates might solubilise less labile mineral P to increase available P (Bünemann, 2015; Hedley et al., 1982; Ziadi et al., 2013). Hence, the citric acid method could help to accurately account for legacy P in the soil including organic P in the P budgeting for long term managed agricultural fields or to minimize P build up in newly established farm soils (Sanderson & Sanderson, 2006).

However, the performance of citric acid in soil B was different than soil A but was similar to Olsen-aP (Table 6. 5). Citric acid only extracted about 50% or less of the available P that could be extracted by Olsen or Mehlich-3 in soil A and B control, which implies the weakness of citric acid to dissolve labile P from the mineral surface or offer better choices to overcome the over-extraction of P by the later methods. The effect of RAS slurry or dairy manure was not observed in soil B as soil B might have more active P-fixing minerals, which could also form organometallic complexes (Grand & Lavkulich, 2015). Thus, more than one P-*test* might be required to quantify the P pools in soils that have been managed differently. In addition, the SOM should be considered as P-test selection criteria in addition to soil pH and soil type.

Additionally, Mehlich-3 extractable available P (Mehlich-3-aP) followed a similar trend and extracted a relatively comparable amount of available P with citric acid. However, Mehlich-3 extracted significantly more available P from soil A treated with RAS slurry without biochar than the same soil treated with biochar, which is opposite to the trend for the citric acid method (Table 6. 5). This is corroborated by the weaker negative correlation ($r = 0.15$) and significant positive correlation ($r = 0.65$) of Mehlich-3-aP with Al and SOC in soil A amended with biochar, respectively (Table S6. 3). Thus, the Mehlich-3 method was not an efficient method to measure available P in soils with high SOC, although a good

correlation was observed between Mehlich-3-aP and SOC (Table S6. 2). The increased SOC might have reduced the adsorption of P on Al hydr(oxides) mineral surfaces as discussed in Chapter 4, which was less extractable with the Mehlich-3 solution designed for mineral soils. Furthermore, Ziadi et al. (2001) suggested finding a method which properly determines available P in the soil, as most of the P-*tests* have a weakness in accounting for organic P in the soil (Ziadi et al., 2001; Ziadi et al., 2013). Also, Cade-Menun et al. (2018) found inconsistent organic P extractability by the Mehlich-3 solution (Cade-Menun et al., 2018). The P measurement in long-term managed fields and soils with higher organic carbon content might require the use of other P-*tests* like citric acid, which accounted for organic P in the soil to reduce the dependence on only inorganic P in agricultural fields (George et al., 2017; Huang et al., 2017) and consequently reduce P build up (Sanderson & Sanderson, 2006).

On the other hand, Mehlich-3 extracted significantly more available P than the Olsen and citric acid methods from soil B, regardless of the P source (Table 6.7) ($p<0.05$) in agreement with baseline P analysis, which supports the above speculation and could be explained by the nature of the Mehlich-3 solution targeting mineral bound P relative to the Olsen and citric acid methods that might target easily desorbed mineral P. Moreover, Mehlich-3-aP has significant negative correlation ($r = 0.68$) with Al and a weaker negative correlation ($r= 0.47$) with Fe content in soil B (Table S6. 4). Hence, the Mehlich-3 method performed better in mineral Podzols but might misinform the P availability index for the newly converted CAFD Podzols.

Additionally, the total P in the same sample was measured in citric acid (citric-tP) and Mehlich-3 (Mehlich-3-tP) extract using ICP-OES. The effect of different P sources, biochar amendment, and soil properties like Al, Fe, and SOC on the citric-tP and Mehlich-3-tP follow a similar trend with the citric-aP and Mehlich-3-aP (Table 6. 5, Table S6. 2, Table S6. 3 and Table S6. 4).

Overall, the agronomic P-*tests* used in this study had similar extraction performances in soil A based on Tukey's test (Table 6. 7). However, Olsen extracted significantly higher available P than Mehlich-3 and citric acid methods ($p<0.05$) when the data from soil A treated with RAS slurry was excluded from the analysis (ANOVA output not presented) while Mehlich-3 extracted significantly more available P than the Olsen and citric acid methods from soil B (Table 6. 7). The Olsen method extracted more available P from soil A with unstable or extractable mineral content while Mehlich-3 extracted more available P from soil B with stable or less extractable minerals. Despite this, citric acid performed better in extracting more available and total soil P from mineral soil with higher SOM or soils from fields under dairy manure management (discussed in Chapter 3). The P analyzed with colorimetric and ICP-OES in Mehlich-3 and citric acid methods have a strong correlation ($r = 0.99$), they can be used for nutrient recommendations based on field calibration. Thus, their interpretation might slightly differ based on soil types, management history, and crop types (Mallarino, 2003).

Also, Olsen and citric acid extractable P concentrations from soil A (without biochar amendment) were significantly higher than soil B (without biochar amendment) ($p<0.05$). This was related to the differences in P adsorption strength of soils A and B, as discussed

in Chapter 4. On the other hand, water and Mehlich-3 extractable P in soil A was not significantly different ($p>0.05$) than in soil B. Mehlich-3 was able to extract a comparable quantity of P from more stable mineral soils (soil B) than Olsen and citric acid methods. Though the chemical properties like pH and Al of the soil are known to control P extractability (Daly et al., 2015), the fertilizer type used might mask the effect of soil A and B properties on P extractability (Wuenscher et al., 2015). Biochar amendment did not affect P extractability by water, Olsen, Mehlich-3, or citric acid in soil A ($P>0.05$).

6.4.3. P Uptake by Tall Fescue Roots and Shoots from Podzols Treated with Different P Sources and Biochar

Table 6. 6 shows the P uptake by the tall fescue root and shoot tissue from soils A and B receiving a uniform P rate from different sources. The P accumulation in the tall fescue roots and shoots from soils A and B was significantly influenced by the P source ($P<0.05$) but not affected by biochar amendment or soil types ($p>0.05$). The P accumulation by the roots grown in soil A receiving different sources of P (110 kg P ha^{-1}) was 2-4 times higher than from the soil A control, while in soil B, it was 3.5-6.0 fold greater than the soil B control. Also, the P uptake by the shoot tissue in the soil A treated with different P sources was 2.5-8.5 times higher than the soil A control, whereas the P uptake by the shoot tissue from soil B treated with different P sources was 2-3 times higher than soil B control. The results demonstrate that P uptake depends on the P sources. In particular, the P uptake by the roots from soils treated with RAS slurry was significantly higher than other P sources and control soils. This could be related to the dynamics of SOM in the RAS slurry, which might improve the soil microbial activities and P availability (White, 2008). Also, the

increased content of SOC increased available P in the soil by reducing the P adsorption and boosting P desorption (Yang et al., 2019). Though this study did not test for various P rates, other studies have reported that an increase of P application rates increased the P uptake in tall fescue root or shoot biomass (Anderson et al., 2014.; Paredes et al., 2011; Sikora et al., 1982). Similarly, the P uptake by the grass increased with increased P rates in a field experiment conducted in Abitibi-Temiscaming, Quebec (Ziadi et al., 2001); the soil I this report had lower Mehlich-3-P compared to the baseline soil P in this study. The P uptake by the Kokanee tall fescue in this study was lower than the P uptake by the Kentucky 31 tall fescue (Sikora et al., 1982). The later study applied higher P application rates (up to 390 kg P ha^{-1}) to the soils compared to this study. Also, in this study, the P uptake by the roots and shoots was not significantly different regardless of the soil types, similar to Sikora and Enkiri (2004) (Sikora & Enkiri, 2004). In contrast, Sikora et al. (1982) reported that P uptake by the shoots was higher than the roots while Sikora and Enkiri (2005) reported the opposite (Sikora et al., 1982; Sikora & Enkiri, 2005). The differences could be related to the differences in soil types, P sources, and overall experimental conditions.

Furthermore, Sikora and Enkiri (2004, 2005) found that the P uptake by the fescue was not affected by the P sources (triple superphosphate and poultry litter compost), but was affected by P rates and soil types (Sikora & Enkiri, 2004, 2005). Similarly, this study noticed no significant ($p>0.05$) differences between the P uptake by the tall fescue from soils treated with mineral fertilizer, dairy manure, and RAS supernatant, but in all cases the uptake was significantly higher than control treatments ($p<0.05$) (Table 6. 6). Thus, the tall fescue was able to extract P from different soil types amended with different P sources and

from control soils; also Paredes et al. (2011) (Paredes et al., 2011) reported that tall fescue was able to take up 67% more P than ryegrass at lower P availability.

Table 6. 4. Post-harvest descriptive statistics of pH, nitrogen, and carbon in the soils A and B. The similar superscript letters in the same column indicate no significant difference at alpha 0.05. The sample size for each means is 5.

	Treatment condittions		*pH*		*Nitrogen, % dry*		*Total Carbon, % dry*		*Organic Carbon, % dry*		*Ammonium-N, mg N kg^{-1}*		*Nitrate-N, mg N kg^{-1}*	
Soil types	P sources	Biochar	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Soil-A	Control-A	No	5.62^{a}	0.04	0.07^{a}	4.47×10^{-3}	0.94^{a}	0.03	0.93^{a}	3.48×10^{-2}	1.14	0.38	0.69^{a}	0.20
	Mineral	No	4.96^{b}	0.25	0.09^{b}	4.47×10^{-3}	1.22^{b}	0.05	1.20^{a}	4.66×10^{-2}	1.35	0.37	8.57^{a,b}	9.37
	Dairy	No	5.74^{a,c}	0.05	0.10^{b}	1.10×10^{-3}	1.49^{b}	0.31	1.47^{c}	3.07×10^{-1}	1.66	0.66	0.10^{a}	0.10
	Slurry	No	5.68^{a}	0.24	0.10^{b,c}	8.37×10^{-3}	1.22 ^{a,b}	0.04	1.20^{a,}	3.91×10^{-2}	2.90	0.37	18.48^{b}	23.09
	Supernatant	No	5.58^{a}	0.04	0.09^{a,b}	8.94×10^{-3}	1.21^{a,b}	0.05	1.19^{a}	4.30×10^{-2}	1.89	0.14	0.24^{a}	0.27
	Mineral	Yes	5.48^{a}	0.04	0.09^{b}	8.94×10^{-3}	3.15^{c}	0.20	3.13^{b}	2.01×10^{-1}	1.65	0.56	1.07^{a,b}	1.94
	Dairy	Yes	6.02^{c}	0.04	0.10^{b}	5.48×10^{3}	3.02^{c}	0.19	3.00^{b}	1.97×10^{-1}	1.09	0.18	0.40^{a}	0.26
	Slurry	Yes	5.62^{a}	0.16	0.12^{c}	8.94×10^{-3}	3.40^{c}	0.08	3.37^{b}	7.36×10^{-2}	0.67	0.18	12.79^{a,b}	15.37
	Supernatant	Yes	5.86^{c}	0.05	0.10^{b}	8.94×10^{-3}	3.20^{c}	0.12	3.18^{b}	1.17×10^{-1}	0.25	0.14	0.44^{a}	0.19
Soil-B	Control-B	No	5.86^{c}	0.05	0.05^{d}	5.48×10^{-3}	0.62^{d}	0.03	0.61^{d}	3.28×10^{-2}	0.42	0.26	0.44^{a}	0.12
	Mineral	No	5.04^{b}	0.05	0.06^{a,d}	5.48×10^{-3}	0.69^{a,d}	0.03	0.68^{a,d}	2.65×10^{-2}	0.58	0.43	5.21^{a,b}	1.75
	Dairy	No	6.10^{c}	0.10	0.07^{a,d}	4.47×10^{-3}	0.72^{a,d}	0.09	0.70^{a,d}	8.59×10^{-2}	BDL	BDL	0.33^{a}	0.27
	Slurry	No	5.16^{b}	0.15	0.06^{a,d}	5.48×10^{-3}	0.64^{d}	0.04	0.63^{d}	4.03×10^{-2}	0.39	0.30	7.43^{a,b}	5.38
	Supernatant	No	5.60^{a}	0.07	0.07^{a,d}	4.47×10^{-3}	0.68^{a,d}	0.06	0.67^{a,d}	6.17×10^{-2}	0.13	0.19	0.37^{a}	0.17

Below detection limit (BDL)

Table 6. 5. Post-harvest descriptive statistics of soil P extracted by water, citric acid, Mehlich-3, and Olsen as analyzed by colorimetric (Col) and inductively coupled plasma optical emission spectrometry (ICP-OES). The similar superscript letters in the same column indicate no significant difference at alpha 0.05. The unit of mean and standard deviation (STD) is (mg P kg^{-1}) and the sample size for each means is 3.

Soil types	P sources	Biochar	Water-Col		Olsen- Col		Citric acid-Col		Mehlich-3-Col		Citric acid-ICP		Mehlich-3-ICP	
			Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Soil-A	Control-A	No	0.31^{a}	0.02	27.33^{a}	2.08	13.14^{a}	0.62	20.49^{a}	2.02	20.93^{a,c}	2.01	22.84^{a}	0.55
	Mineral	No	0.27^{a}	0.00	36.33^{b}	0.58	27.22^{a,b}	4.12	26.61^{b}	1.78	37.93^{a}	3.98	28.32^{b}	0.92
	Dairy	No	0.39^{a}	0.09	38.00^{b}	1.73	28.57^{b}	3.05	27.20^{b}	1.27	35.38^{a}	3.46	28.54^{b}	0.94
	RAS Slurry	No	0.33^{a}	0.04	61.00^{c}	2.65	84.23^{c}	8.17	67.80^{c}	0.57	92.98^{b}	10.16	65.21^{c}	1.26
	RAS Supernatant	No	0.32^{a}	0.08	38.67^{b}	1.15	32.36^{b}	4.57	29.24^{b}	2.61	34.82^{a}	4.67	30.33^{b}	1.84
	Mineral	Yes	0.27^{a}	0.00	34.67^{b}	1.53	27.76^{a,b}	2.85	27.33^{b}	1.09	35.32^{a}	3.71	28.69^{b}	0.83
	Dairy	Yes	0.44^{a}	0.12	33.33^{b}	0.58	32.36^{b}	9.14	27.20^{b}	0.80	35.62^{a}	10.32	27.17^{a}	1.72
	RAS Slurry	Yes	0.43^{a}	0.02	61.00^{c}	1.00	101.56^{d}	5.98	53.92^{d}	3.94	110.94^{b}	5.26	52.82^{d}	3.33
	RAS Supernatant	Yes	0.30^{a}	0.00	39.67^{b}	0.58	29.52^{b}	1.43	30.75^{b,e}	2.03	33.10^{a}	2.00	30.64^{b}	0.90
Soil-B	Control-B	No	0.28^{a}	0.02	20.00^{d}	0.00	11.92^{a}	0.94	28.58^{b,e,f}	0.63	11.71^{c}	0.83	27.27^{e}	0.76
	Mineral	No	0.32^{a}	0.08	26.33^{e}	2.08	31.15^{b}	7.60	33.58^{e,f}	4.05	36.21^{d}	11.38	32.49^{f}	2.81
	Dairy	No	0.30^{a}	0.00	22.67^{d}	0.58	22.75^{a,b}	4.00	36.22^{e}	1.19	25.04^{c,d}	4.05	34.55^{f}	0.58
	RAS Slurry	No	0.33^{a}	0.11	22.33^{d}	0.58	26.27^{a,b}	2.88	35.49^{e}	1.19	31.59^{d}	4.50	33.20^{f}	0.31
	RAS Supernatant	No	0.30^{a}	0.03	33.00^{e}	2.00	37.65^{b}	5.63	45.10^{g}	0.50	38.61^{d}	7.69	42.09^{g}	1.37

Table 6. 6. Mean and standard deviation (STD) of P uptake by the tall fescue root and shoot tissue from soil A and B treated with different P sources. The similar superscript letters in the column indicate no significant difference at alpha 0.05. The sample size for each means is 3.

Soil types	P sources	Biochar	%P, Dry Root		Dry Root, g pot^{-1}		P, mg pot-1 (root)		%P, Dry Shoot		Dry Shoot, g pot^{-1}		P, mg pot-1 (shoot)		DM Shoot, t ha^{-1}	
			Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Soil-A	Control-A	No	0.10	0.01	3.83	0.29	3.88^{a}	0.21	0.09	0.01	2.67	1.61	2.48^{a}	1.88	0.85^{a}	0.00
	Mineral	No	0.14	0.02	7.33	2.75	9.88^{b}	2.87	0.14	0.03	6.67	2.93	8.83^{b}	2.53	3.11^{b}	0.56
	Dairy	No	0.10	0.01	8.67	2.89	8.82^{b,c}	3.28	0.10	0.02	8.67	0.29	8.73^{b}	2.04	4.90^{c}	0.16
	Slurry	No	0.24	0.01	7.00	1.50	16.79^{d}	2.91	0.21	0.02	10.33	1.26	21.37^{c}	4.00	6.69^{d}	1.70
	Supernatant	No	0.12	0.03	5.83	1.44	6.66^{c}	1.51	0.10	0.03	6.17	4.04	5.21^{d}	2.74	4.80^{c}	0.56
	Mineral	Yes	0.10	0.01	7.33	2.02	7.40^{e}	2.42	0.09	0.01	9.00	3.50	7.95^{e}	3.16	5.56^{e}	0.43
	Dairy	Yes	0.11	0.01	6.83	2.08	7.64^{e}	2.11	0.10	0.01	8.33	1.04	7.79^{e}	0.58	4.52^{f}	0.28
	Slurry	Yes	0.17	0.02	8.33	4.04	14.05^{f}	7.67	0.17	0.03	9.17	0.76	15.84^{f}	4.04	7.06^{g}	0.56
	Supernatant	Yes	0.11	0.01	9.50	1.80	10.19^{e,f}	3.18	0.08	0.03	8.33	1.15	6.31^{e}	2.72	4.90^{f}	0.86
Soil-B	Control-B	No	0.09	0.02	2.67	0.58	2.25^{g}	0.31	0.07	0.01	4.33	5.35	3.09^{g}	3.68	0.94^{h}	0.16
	Mineral	No	0.12	0.01	7.83	2.57	9.74^{h,i}	3.52	0.12	0.01	8.83	1.04	10.42^{h}	1.98	4.80^{i}	0.56
	Dairy	No	0.07	0.01	12.00	3.04	8.28^{h}	1.62	0.08	0.01	9.83	2.31	7.98^{h,i}	2.42	5.93^{j}	1.13
	Slurry	No	0.08	0.01	17.33	2.25	13.33^{j}	3.66	0.07	0.01	8.00	1.32	5.52^{g,i}	1.53	4.52^{i}	0.75
	Supernatant	No	0.11	0.01	6.50	1.80	7.17^{i}	1.50	0.12	0.02	9.00	0.87	10.50^{h}	2.64	4.99^{i}	0.59

Table 6. 7. Post-Hoc comparison of P extractability in soil A and B subjected different treatments.

P tests		Mean Difference		
		Soil A-No biochar	Soil A-Biochar	Soil B-No biochar
Citric acid-col	Mehlich-3-col	13.00	2.84	-9.85
	Olsen-col	5.64	-3.16	1.08
	Water-col	47.45*	36.78*	25.64*
Mehlich-3-col	Olsen-col	-7.37	-6.00	10.93*
	Water-col	34.44*	33.94*	35.49*
Olsen-col	Water-col	41.81*	39.942*	24.56*
Citric acid-ICP	Mehlich-3-ICP	9.36	18.92	-5.29

*The mean difference is significant at the 0.05 level.

6.4.4. Relationship of Post-harvest Extractable Soil P with the P Uptake by Tall Fescue Roots and Shoots, and Yield of Shoots Dry Mass

Table 6. 8 shows a Pearson correlation between selected soil properties, available and total P in the soil extracted with citric acid, Mehlich-3, Olsen or water, P in the root and shoot tissues, and yield of shoot dry mass for soil A treatments without biochar amendment (n = 15), soil A treatments with biochar amendment (n = 12), and soil B treatments without biochar amendment (n = 15). The available P extracted by citric acid, Mehlich-3, and Olsen had a stronger correlation with (a) tall fescue responses (P uptake in the root and shoot and yield of shoot dry mass) in soil A treatments without biochar amendment, (b) P uptake and yield of shoot dry mass in soil A treatments amended with biochar, and (c) good correlation with P uptake in the shoot biomass in soil B without biochar amendment (Table 6. 8). A stronger correlation was observed between soil P (Mehlich-3-aP, Olsen-aP, and Mehlich-3-tP) and P uptake by both root and shoot biomass from soil A without biochar amendment compared to the correlation reported in Ziadi et al. (2001). In contrast, they reported a

stronger correlation (r = 0.60) between water-extractable P and cumulative P uptake (Ziadi et al., 2001) comparable to the correlation in this study (r = 0.42) for soil A amended with biochar. The difference in the experimental settings might explain the correlation differences. The correlation of available P extracted by citric acid, Mehlich-3, and Olsen with tall fescue responses was affected by biochar amendment and soil types (Table 6. 8). Similarly, other studies have reported a variable correlation between the extractable P in the soil and P uptake in the biomass of grasses (Krogman & Lutwick, 1964; Massey et al., 1970).

The water-aP has a relatively weak correlation (r= 0.42) with P uptake in the shoot from soil A treatments amended with biochar but was not significantly correlated with P uptake in the root and shoot from soil A without biochar amendment. Contrary to this finding, a stronger correlation (r = 0.81) was reported between water extracted P and P uptake in root crops (Kulhánek et al., 2007). This could be related to the differences in crop types and experimental conditions where the data of the latter study was from the long-term field experiment, while the data in this study was from short term (12 weeks) pot experiment and also measure soil at the end of the experiment.

Similarly, the total P extracted with citric acid (citric-tP) and Mehlich-3 (Mehlich-3-tP) have strong correlation with P uptake by root and shoot (r = 0.85-0.95) and yield of shoot dry mass (r= 0.72-0.83), regardless of biochar and P source in soil A treatments but the correlation was slightly decreased in soil B treatments. Hence, the tall fescue had a better physiological response to soil A than soil B regardless of P sources and biochar amendment. Furthermore, Figure S6.1 to Figure S6.9 (supplementary data) and Table 6. 9 show linear regression models to predict tall fescue responses, i.e., P uptake by the roots, and shoots,

and dry mass shoots yield from a post-harvest available soil P extracted by citric acid, Mehlich-3, Olsen, and water methods and total soil P extracted by citric acid and Mehlich-3 methods for the soil groups discussed above. Accordingly, the P uptake (mg P pot^{-1}) of the tall fescue roots in the soil A treatments without biochar amendment could be accurately predicted from available and total P in the post-harvest soils with 69-72% variation explained by the model while only 21-36% variation can be explained in soil A treatments amended with biochar. The Olsen, citric acid, and Mehlich-3 extractable P explained greater than 60% of the variation in P uptake in the shoots. Thus, biochar might be a sink for available P, reducing the P availability to the roots in soil A as observed from the relation. Generally, a lower coefficient of determination (R^2) was calculated for tall fescue responses predicted from extractable P in the soil B treatments (Table 6. 9). Overall, the slope of P uptake in the root and shoot was less than one for the available and total P extracted in the post-harvest soils by agronomic P-tests (citric acid, Mehlich-3, Olsen), which indicates higher P removed by the tall fescue from the soils. The P uptake from soil B was also lower than soil A as observed from the models. In most treatment conditions, the water-aP explained less than 10% the variation of tall fescue responses (Table 6. 9). While a field study reported better R^2 (0.66) for P uptake in the root crops predicted from water-extractable P (Kulhánek et al., 2007), the reason for a lower R^2 in this study could be due to the lower water-aP in the newly converted soils A and B. On the other hand, a better R^2 was obtained for P uptake predicted from Mehlich-3-aP and Olsen-aP compared to the same study (Kulhánek et al., 2007). Hamel and Heckman (Hamel & Heckman, 2006) reported an R^2 of 0.61 for tall fescue shoot yield from Mehlich-3-tP while in this study an R^2 of 0.52 was obtained for soil A without biochar amendment and an R^2 of 0.66 for soil A

amended with biochar. Also, a long-term field study from Ireland reported a stable non-linear regression coefficient (R^2 = 0.90) for grass yield with Morgan-P (Tunney, 2002). Additionally, Messiga et al. (2015) reported a linear relation between Mehlich-3-P and P budgeting (R^2 = 0.71) in soils of Levis, Quebec, Canada (Messiga et al., 2015) comparable to the relation between Mehlich-3-tP and P uptake in the root in soil A treatments without biochar amendment (R^2 = 0.70) in this study. Overall, citric acid, Olsen and Mehlich-3 have a comparable relationship with dry mass shoot yield. However, field or pilot calibration is required to confirm the relationships observed in this study using various P application rates and plant responses in NL soil and environmental conditions.

Table 6. 8. Pearson correlation of soil properties, post-harvest available and total soil P, P uptake in the tall fescue roots and shoots, and yield of shoot dry mass for soils A and B.

Soil type	Soil properties	P uptake (mg P pot^{-1})		Shoot-Yield (t ha^{-1})
		Root	Shoot	
Soil A-No Biochar (n=15)	pH	-0.14	-0.01	0.34
	OC	0.18	0.19	0.46
	Fe	0.66	0.65	0.58
	Al	-0.61	-0.64	-0.89
	CA-Col	0.83	0.86	0.79
	M3-Col	0.83	0.90	0.73
	OS-Col	0.85	0.93	0.81
	DW-Col	0.18	0.07	0.40
	CA-ICP	0.84	0.87	0.76
	M3-ICP	0.84	0.91	0.72
Soil A-Biochar (n=12)	pH	-0.35	-0.44	-0.50
	OC	0.54	0.72	0.57
	Fe	0.31	0.66	0.90
	Al	-0.25	-0.07	0.35
	CA-Col	0.47	0.80	0.82
	M3-Col	0.59	0.84	0.79
	OS-Col	0.60	0.79	0.80
	DW-Col	0.21	0.42	0.12
	CA-ICP	0.46	0.80	0.83
	M3-ICP	0.59	0.83	0.81
Soil B-No Biochar (n=15)	pH	-0.56	-0.25	-0.06
	OC	0.12	0.23	0.55
	Fe	-0.23	-0.04	-0.31
	Al	-0.25	-0.31	-0.66
	CA-Col	0.48	0.65	0.59
	M3-Col	0.23	0.61	0.57
	OS-Col	0.07	0.69	0.42
	DW-Col	-0.08	0.26	0.16
	CA-ICP	0.57	0.55	0.65
	M3-ICP	0.20	0.64	0.62

Table 6. 9. Linear regression equations established for P uptake (mg P pot^{-1}) by tall fescue roots and shoots, dry mass (DM) shoots yield from available and total P in soil A and B extracted with citric acid (CA), Mehlich-3 (M3), Olsen, and water methods.

Soil type	Roots P uptake	R^2	Shoots P uptake	R^2	DM shoots yield	R^2
Soil A-No Biochar (n=15)	0.16*CA-aP + 3.29	0.69	0.45*CA-aP - 3.14	0.75	0.07*CA-aP + 1.97	0.63
	0.23*M3-aP + 1.28	0.69	0.36*M3-aP + 1.28	0.82	0.09*M3-aP + 1.03	0.53
	0.36*Olsen-aP -5.28	0.72	0.57*Olsen-aP -13.57	0.87	0.15*Olsen-aP -1.97	0.65
	17.78*water-aP + 3.43	0.05	9.91*water-aP + 6.10	0.01	13.47*water-aP -0.31	0.15
	0.16*CA-tP + 2.20	0.71	0.24*CA-tP – 1.12	0.76	0.06*CA-tP + 1.29	0.58
	0.26*M3-tP + 0.14	0.70	0.41*M3-tP – 4.95	0.83	0.10*M3-tP + 0.64	0.52
Soil A- Biochar (n=12)	0.07*CA-aP + 6.57	0.22	0.11*CA-aP + 4.11	0.63	0.03*CA-aP + 4.17	0.67
	0.24*M3-aP + 1.58	0.35	0.33*M3-aP -2.02	0.71	0.0.08*M3-aP + 2.88	0.62
	0.24*Olsen-aP -0.40	0.36	0.31*Olsen-aP -3.73	0.62	0.0.08*Olsen-aP + 2.23	0.65
	10.21*water-aP + 6.16	0.04	20.33*water-aP -2.19	0.17	1.33*water-aP + 5.03	0.01
	0.06*CA-tP + 6.47	0.21	0.11*CA-tP + 3.81	0.63	0.03*CA-tP + 4.06	0.70
	0.25*M3-tP + 1.01	0.35	0.35*M3-tP – 2.68	0.70	0.08*M3-tP + 2.62	0.66
Soil B-No Biochar (n=15)	0.21*CA-aP + 2.68	0.23	0.24*CA-aP + 1.14	0.43	0.11*CA-aP + 1.33	0.34
	0.17*M3-aP + 2.05	0.05	0.38*M3-aP – 6.27	0.37	0.19*M3-aP - 2.41	0.33
	0.06*Olsen-aP + 6.61	0.01	0.53*Olsen-aP – 5.61	0.48	0.16*Olsen-aP + 0.16	0.18
	19.83*water-aP + 2.09	0.07	-7.84*water-aP + 9.90	0.01	8.83*water-aP + 1.54	0.07
	0.21*CA-tP + 2.11	0.32	0.17*CA-tP + 2.49	0.30	0.11*CA-tP + 1.19	0.43
	0.17*M3-tP + 2.32	0.04	0.46*M3-tP - 8.10	0.41	0.23*M3-tP – 3.52	0.39

6.5. Conclusions

In this study, the effect of P sources (mineral fertiliser, dairy manure, RAS slurry and supernatant) and biochar amendment on the soil P extractability with four P-*tests*, P uptake by tall fescue root and shoot biomass, and yield of shoot dry mass were investigated. Additionally, a linear relationship was established between plant responses measured as P uptake and yield of shoot dry mass and soil P extracted with the P-*tests*. The following conclusions were drawn from this study:

- Olsen extracted significantly more P from soil A than soil B while Mehlich-3 performed the opposite, indicating better applicability in mineral soils despite overestimation of P availability in mineral soils.

- Citric acid extracted significantly higher available and total P in soils treated with RAS slurry compared to Olsen and Mehlich-3, which might be a good candidate to measure available, organic, and total P in soils rich in organic carbon.

- The environmental P-*test* (water-extractable P) extracted less than 0.5 mg P kg^{-1} of soil regardless of soil type, P sources, and biochar amendment, which indicated the newly converted CAFD soils demonstrated no risk of P loss, but this finding is not conclusive before field confirmation.

- All the tested P-*tests* except water-P have better linear relations with P uptake in the tall fescue roots and shoots and yield of shoot dry matter for soil A than soil B.

- The RAS slurry, which was rich in SOM and nutrients, showed better plant performance compared to mineral fertiliser, dairy manure, and RAS supernatant. Thus, further investigating must be conducted to evaluate RAS slurry performance at pilot-scale for further recommendation.

- Soil amended with biochar or organic fertiliser (dairy manure or RAS slurry) improved soil properties like soil pH, SOM, and available P but not P uptake. Thus, as biochar was very a expensive product compared to fertilizer (Latawiec et al., 2019), it might not be economical in the establishment of tall fescue on recently converted Podzols.

6.6. References

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6.7. Supplementary Material

Table S6.1. The mean and standard deviation (STD) of selected nutrients in the post-harvest soils extracted with Mehlich-3, citric acid, and ammonium acetate (NH4-acetate) solutions. The sample size for each measurement was 3.

Extraction methods	Element		Soil A									Soil B				
		Treat. ID	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14
		Fertiliser	None	Mineral		Dairy		RAS Slurry		RAS Supernatant		None	Mineral	Dairy	RAS Slurry	RAS Supernatant
		Biochar	No	No	Yes	No	Yes	No	Yes	No	Yes	No				
Mehlich-3	Ca	Mean	28.99	91.86	66.29	73.03	625.51	74.34	160.95	430.58	199.70	340.93	23.39	82.80	45.06	84.57
		STD	1.50	50.90	50.54	1.55	312.31	5.31	2.77	9.89	11.98	549.57	3.81	3.23	2.28	5.27
	Mg	Mean	3.93	3.45	2.10	12.44	3.06	2.38	16.70	6.88	6.81	3.13	-0.17	15.58	0.61	0.98
		STD	2.00	1.40	1.91	0.43	1.66	0.67	0.51	1.72	1.10	0.14	0.28	0.94	0.16	0.57
	K	Mean	40.78	44.66	39.36	57.55	17.98	21.03	105.60	40.96	49.18	37.99	21.24	58.21	20.44	15.84
		STD	0.85	7.24	16.11	4.93	1.67	1.30	2.38	4.49	4.20	0.34	0.99	9.48	0.66	0.70
	Fe	Mean	69.32^{a}	76.47^{b}	78.50^{b}	78.35^{b}	77.84^{b}	72.98^{a}	68.72^{a}	86.29^{c}	69.64^{a}	56.26^{d}	58.01^{d}	52.08^{d}	53.26^{d}	53.84^{d}
		STD	4.23	2.58	3.86	0.71	1.32	1.48	1.32	2.23	0.42	1.20	2.53	0.13	1.43	2.77
	Na	Mean	2.39	3.30	2.67	23.01	4.67	2.72	23.25	5.63	5.06	1.82	0.88	24.40	1.21	2.08
		STD	0.15	0.74	0.92	1.00	0.66	0.23	0.43	0.34	0.35	0.40	0.19	1.93	0.58	0.60
	Al	Mean	1753^{a}	1727^{a}	1708^{a}	1641^{b}	1563^{b}	1617^{b}	1576^{b}	1617^{b}	1594^{b}	1605^{c}	1595^{c}	1468^{d}	1539^{d}	1506^{d}
		STD	28	29	25	24	21	13	32	33	11	21	29	6	13	14
Citric acid	Ca	Mean	64.26	81.64	167.61	118.39	642.51	123.78	230.21	582.41	254.15	59.32	61.59	125.96	89.41	132.42
		STD	0.63	12.88	5.81	5.43	37.35	10.80	43.91	10.95	5.38	1.82	6.77	6.06	4.92	10.64
	Mg	Mean	8.41	6.98	10.27	19.08	9.22	9.07	26.18	13.09	12.58	9.05	5.28	23.82	6.03	6.72
		STD	0.23	0.55	0.35	0.58	1.18	1.83	5.18	1.97	0.36	0.25	1.03	0.64	0.27	0.82
	K	Mean	63.55	44.82	76.60	88.61	26.52	31.45	173.02	56.18	78.52	54.98	31.57	94.29	31.65	24.13
		STD	1.33	5.90	6.69	6.71	1.76	1.55	40.82	12.06	4.21	1.34	3.30	12.44	1.29	1.28
	Fe	Mean	234.94	259.98	247.21	269.72	255.77	253.43	289.78	291.51	240.10	150.60	243.11	207.47	214.24	218.72
		STD	16.07	15.95	19.26	33.51	22.74	24.41	72.53	17.94	14.61	10.00	62.76	30.14	35.87	46.37
	Na	Mean	11.31	10.32	11.73	34.90	13.88	12.54	40.45	15.11	13.96	10.33	10.84	42.66	10.93	17.21
		STD	0.65	0.99	0.60	1.24	0.55	0.87	9.35	0.84	0.33	1.05	2.38	1.45	0.74	8.07
	Al	Mean	2256	2414	2248	2384	2205	2248	2407	2367	2053	1532	2280	1975	2085	1996
		STD	94	42	119	180	119	122	564	72	80	63	392	139	210	201
NH4-Acetate	Mg	Mean	10.43	8.05	10.76	17.80	8.76	9.60	24.20	12.40	15.40	10.08	7.40	27.60	7.65	9.60
		STD	3.10	1.20	3.05	2.39	1.15	3.03	1.64	1.34	2.79	1.29	0.28	1.82	0.31	1.58
	K	Mean	75.00	37.00	93.40	106.00	17.75	25.40	224.00	52.20	93.20	84.00	26.80	138.00	21.60	13.50
		STD	7.87	8.46	17.87	10.84	2.63	4.51	18.17	15.69	11.50	1.58	2.39	19.24	4.10	1.73

*the sample size (N) for all soils extracted with ammonium acetate was 5. A similar letter in the row shows no significant difference at alpha 0.05.

Table S6. 2. Pearson correlation between selected soil properties, P availability, P uptake by root and shoot, yield of root and shoot in soil A treatments not amended with biochar.

Parameters	Citric-aP	Mehlich-3-aP	Ols-aP	Water-aP	Citric-tP	M3-tP	Shoot-P	Root yield	Shoot yield	Chlorophyll	P-uptake (root)	P-uptake (shoot)	Root-P
pH	0.246	0.226	0.146	.543*	0.202	0.210	-0.131	-0.172	0.326	-0.151	-0.074	0.040	0.094
SOC	-0.084	-0.102	-0.100	-0.226	-0.076	-0.103	-0.215	0.181	0.404	0.060	-0.079	-0.045	-0.224
Fe	0.340	0.329	0.430	0.049	0.349	0.341	0.288	.608**	.607**	.602*	.489*	.510*	0.197
Al	-.797**	-.762**	-.822**	-0.434	-.740**	-.750**	-.574*	-0.274	-.748**	-.656**	-.648**	-.664**	-.681**
Citric-aP	1	.978**	.958**	0.189	.994**	.976**	.826**	0.178	.722**	.680**	.814**	.855**	.938**
Mehlich-3-aP	.978**	1	.965**	0.140	.972**	.999**	.841**	0.165	.654**	.605*	.826**	.905**	.932**
Ols-aP	.958**	.965**	1	0.154	.941**	.968**	.841**	0.243	.713**	.726**	.837**	.921**	.885**
Water-aP	0.189	0.140	0.154	1	0.170	0.141	-0.104	.486*	0.280	0.160	0.259	0.121	0.034
Citric-tP	.994**	.972**	.941**	0.170	1	.970**	.842**	0.183	.696**	.683**	.824**	.861**	.946**
M3-tP	.976**	.999**	.968**	0.141	.970**	1	.841**	0.170	.646**	.603*	.829**	.908**	.928**
Shoot-P	.826**	.841**	.841**	-0.104	.842**	.841**	1	0.082	0.381	.614**	.774**	.825**	.930**
Root yield	0.178	0.165	0.243	.486*	0.183	0.170	0.082	1	0.404	.577*	.623**	0.380	0.072
Shoot yield	.722**	.654**	.713**	0.280	.696**	.646**	0.381	0.404	1	.712**	.588*	.614**	.510*
Chlorophyll	.680**	.605*	.726**	0.160	.683**	.603*	.614**	.577*	.712**	1	.760**	.690**	.601*
P-uptake (root)	.814**	.826**	.837**	0.259	.824**	.829**	.774**	.623**	.588*	.760**	1	.885**	.806**
P-uptake (shoot)	.855**	.905**	.921**	0.121	.861**	.908**	.825**	0.380	.614**	.690**	.885**	1	.818**
Root-P	.938**	.932**	.885**	0.034	.946**	.928**	.930**	0.072	.510*	.601*	.806**	.818**	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table S6. 3. Pearson correlation between selected soil properties, P availability, P uptake by root and shoot, yield of root and shoot in soil A treatments amended with biochar.

Parameters	Citric-aP	Mehlich-3-aP	Ols-aP	Water-aP	Citric-tP	M3-tP	Shoot-P	Root yield	Shoot yield	Chloro.phyll	P-uptake (root)	P-uptake (shoot)	Root-P
pH	-0.260	-0.327	-0.322	0.330	-0.309	-0.365	-0.353	-0.263	-0.498	-0.092	-0.353	-0.439	-0.212
SOC	0.541	.653*	.649*	0.289	0.551	.634*	.588*	0.424	0.570	0.472	0.539	.717**	0.514
Fe	.778**	.767**	.758**	0.115	.808**	.795**	.693*	-0.044	.902**	0.499	0.312	.665*	.656*
Al	-0.117	-0.149	-0.112	-0.419	-0.068	-0.106	-0.104	-0.146	0.354	-0.209	-0.251	-0.069	-0.303
Citric-aP	1	.956**	.959**	0.423	.998**	.960**	.869**	-0.007	.817**	.791**	0.473	.796**	.907**
Mehlich-3-aP	.956**	1	.975**	0.378	.955**	.997**	.876**	0.152	.790**	.772**	.592*	.842**	.928**
Ols-aP	.959**	.975**	1	0.342	.957**	.977**	.821**	0.197	.804**	.785**	.599*	.789**	.885**
Water-aP	0.423	0.378	0.342	1	0.408	0.326	0.441	-0.016	0.110	0.523	0.201	0.407	0.427
Citric-tP	.998**	.955**	.957**	0.408	1	.961**	.866**	-0.019	.835**	.784**	0.462	.795**	.897**
M3-tP	.960**	.997**	.977**	0.326	.961**	1	.870**	0.148	.812**	.754**	.593*	.834**	.931**
Shoot-P	.869**	.876**	.821**	0.441	.866**	.870**	1	0.143	.751**	.684*	0.574	.938**	.837**
Root yield	-0.007	0.152	0.197	-0.016	-0.019	0.148	0.143	1	-0.119	-0.069	.836**	0.306	0.216
Shoot yield	.817**	.790**	.804**	0.110	.835**	.812**	.751**	-0.119	1	.617*	0.220	.646*	.603*
Chlorophyll	.791**	.772**	.785**	0.523	.784**	.754**	.684*	-0.069	.617*	1	0.288	.712**	.646*
P-uptake (root)	0.473	.592*	.599*	0.201	0.462	.593*	0.574	.836**	0.220	0.288	1	.669*	.689*
P-uptake (shoot)	.796**	.842**	.789**	0.407	.795**	.834**	.938**	0.306	.646*	.712**	.669*	1	.813**
Root-P	.907**	.928**	.885**	0.427	.897**	.931**	.837**	0.216	.603*	.646*	.689*	.813**	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

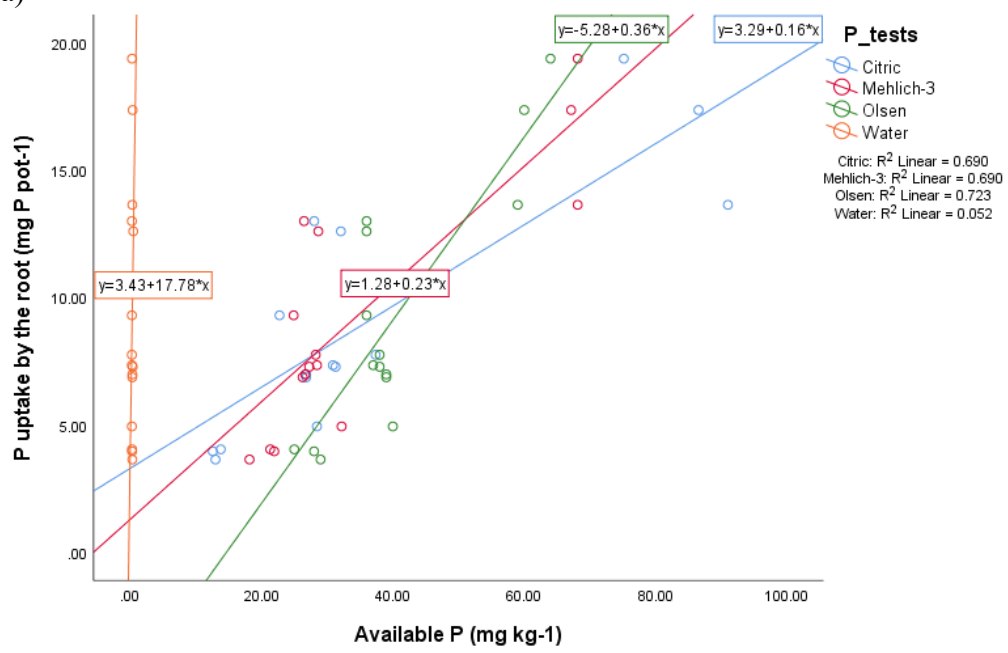
Table S6. 4. Pearson correlation between selected soil properties, P availability, P uptake by root and shoot, yield of root, and shoot in soil B treatments not amended with biochar.

Parameters	Citric-aP	Mehlich-3-aP	Ols-aP	Water-aP	Citric-tP	M3-tP	Shoot-P	Root yield	Shoot yield	Chlorophyll	P-uptake (root)	P-uptake (shoot)	Root-P
pH	-0.411	-0.002	-0.210	-0.151	-0.478	-0.003	-0.345	-0.270	-0.057	-0.493	-0.562*	-0.248	-.546*
SOC													
Fe	0.073	-0.468	-0.105	0.165	0.179	-0.442	0.294	-0.448	-0.312	-0.126	-0.228	-0.040	0.463
Al	-0.256	-0.682**	-0.312	0.122	-0.173	-.672**	0.045	-0.428	-.659**	-0.413	-0.251	-0.312	0.368
Citric-aP	1	0.689**	0.729**	0.320	0.955**	0.710**	0.652**	0.214	0.587*	0.761**	0.483	0.653**	0.522*
Mehlich-3-aP	0.689**	1	0.865**	-0.123	0.532*	0.989**	0.475	0.154	0.575*	0.575*	0.231	0.608*	0.247
Ols-aP	0.729**	0.865**	1	-0.065	0.567*	0.891**	0.759**	-0.176	0.423	.551*	0.070	0.695**	0.657**
Water-aP	0.320	-0.123	-0.065	1	0.453	-0.067	-0.060	0.229	0.258	0.298	0.263	-0.121	0.012
Citric-tP	0.955**	0.532*	0.567*	0.453	1	0.562*	0.510	0.336	0.652**	0.807**	0.566*	0.547*	0.427
M3-tP	0.710**	0.989**	0.891**	-0.067	0.562*	1	0.521*	0.124	0.622*	0.611*	0.205	0.638*	0.288
Shoot-P	0.652**	0.475	0.759**	-0.060	0.510	0.521*	1	-0.305	0.221	0.448	0.064	0.785**	0.840**
Root yield	0.214	0.154	-0.176	0.229	0.336	0.124	-0.305	1	0.549*	0.546*	0.884**	0.091	-0.424
Shoot yield	0.587*	0.575*	0.423	0.258	0.652**	0.622*	0.221	0.549*	1	0.850**	0.533*	0.530*	-0.001
Chlorophyll	0.761**	0.575*	0.551*	0.298	0.807**	0.611*	0.448	0.546*	0.850**	1	0.717**	0.624*	0.323
P-uptake (root)	0.483	0.231	0.070	0.263	0.566*	0.205	0.064	.884**	0.533*	0.717**	1	0.315	0.018
P-uptake (shoot)	0.653**	0.608*	.695**	-0.121	.547*	.638*	.785**	0.091	.530*	.624*	0.315	1	0.465
Root-P	0.522*	0.247	.657**	0.012	0.427	0.288	.840**	-0.424	-0.001	0.323	0.018	0.465	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

(a)



(b)

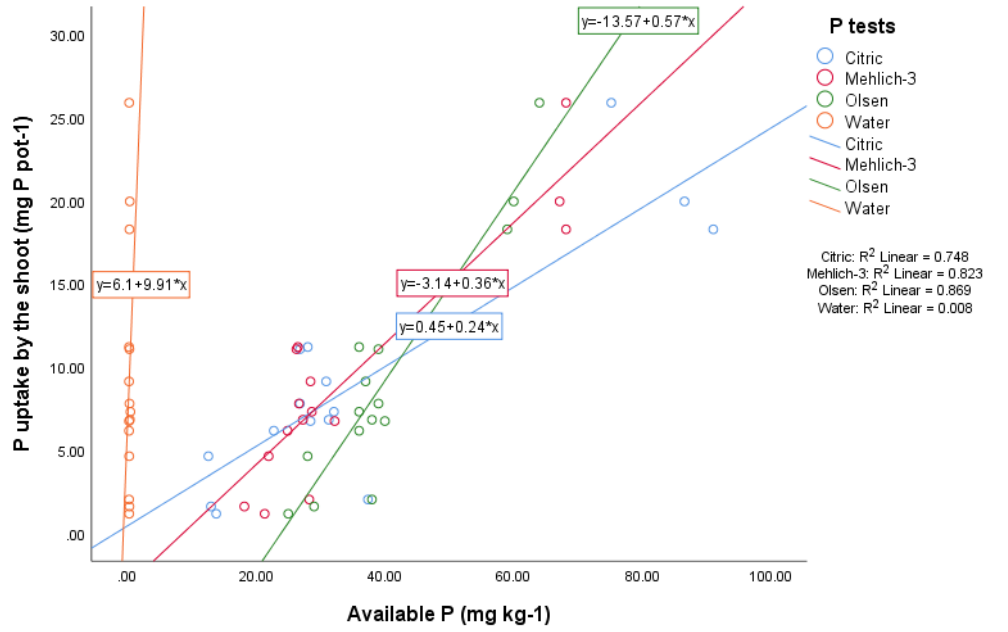
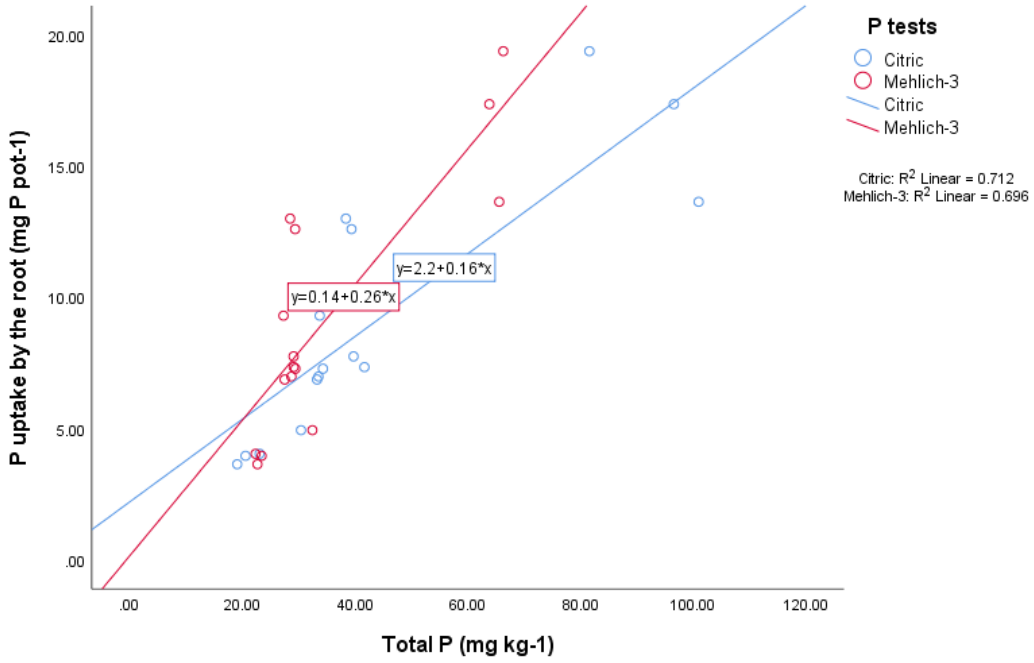


Figure S6.1. Relationship between P uptake by the tall fescue roots (a) and shoots(b) from soil A treated with different P sources (without biochar amendment) versus post-harvest available P in the soil extracted by citric acid, Mehlich-3, Olsen, and water methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



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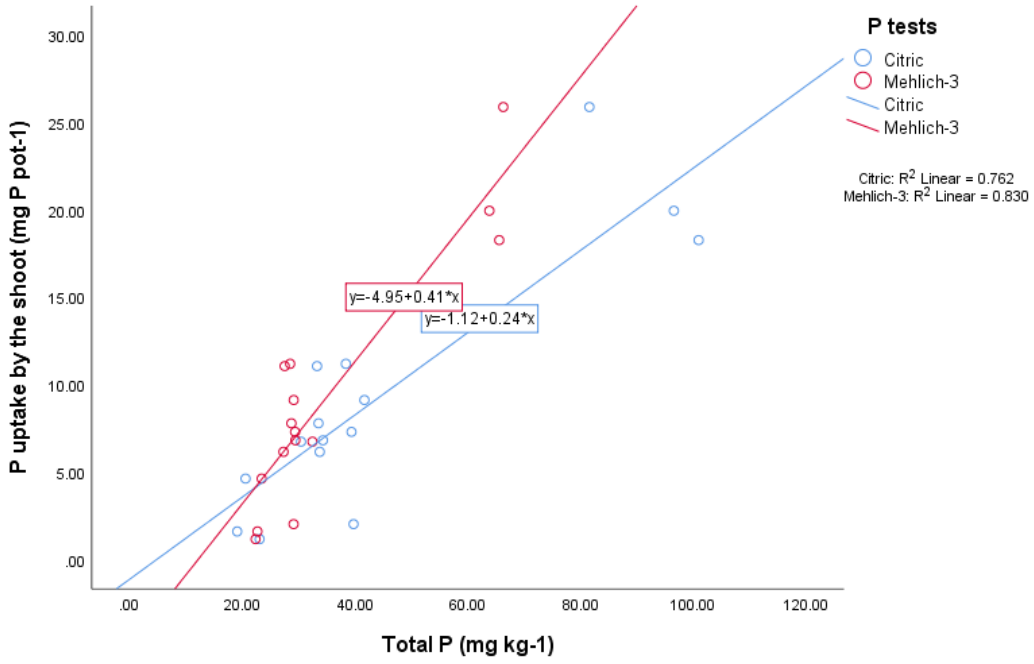
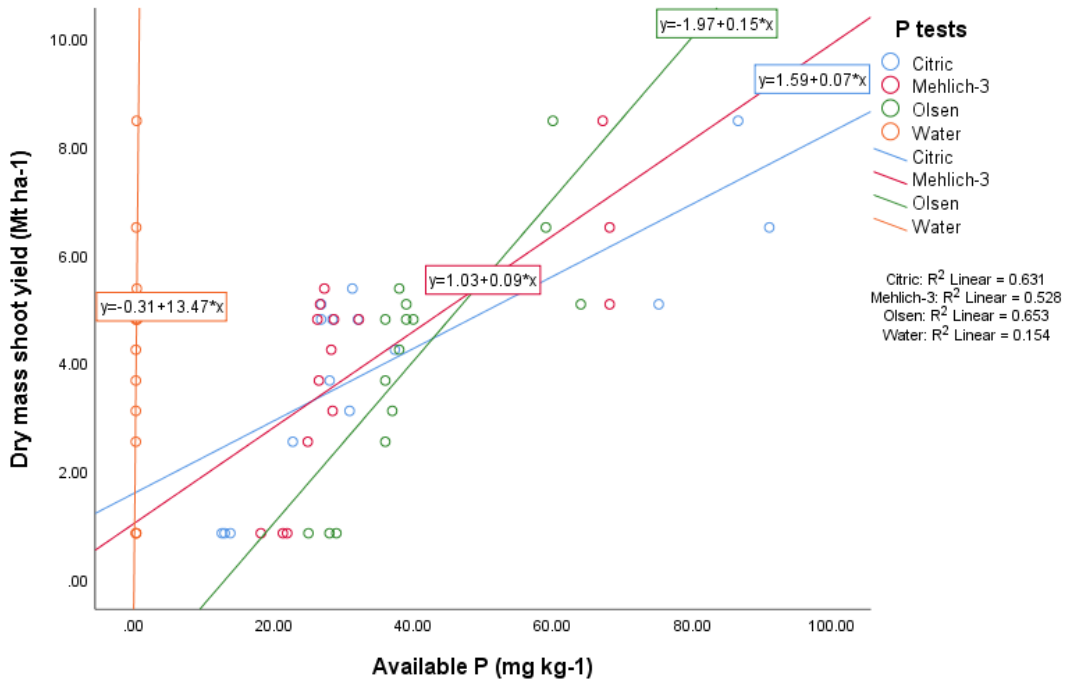


Figure S6.2. Relationship between P uptake by the tall fescue roots (a) and shoots(b) from soil A treated with different P sources (without biochar amendment) versus post-harvest total P in the soil extracted by citric acid, and Mehlich-3 methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

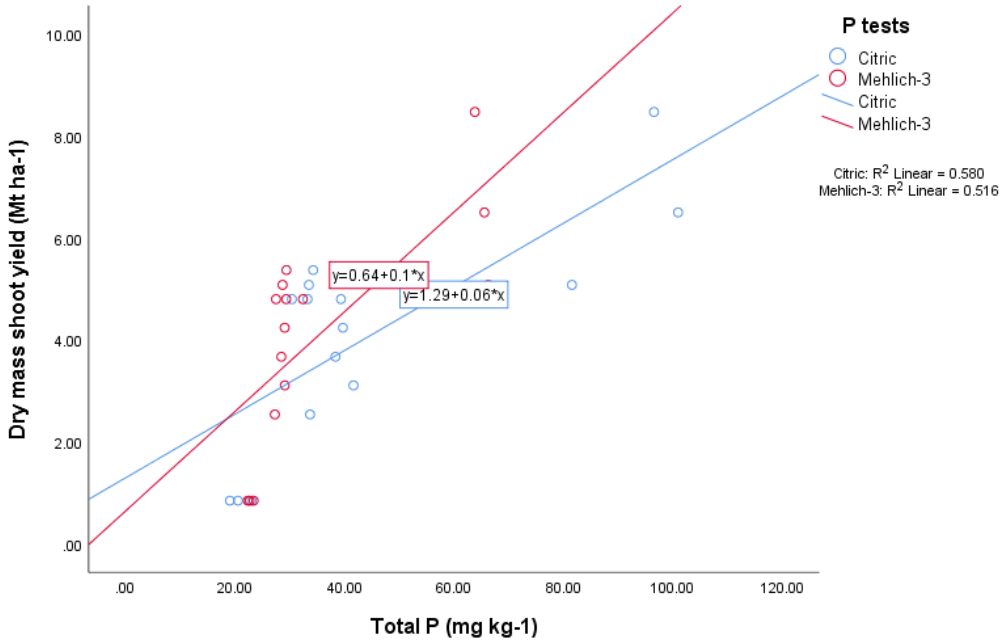
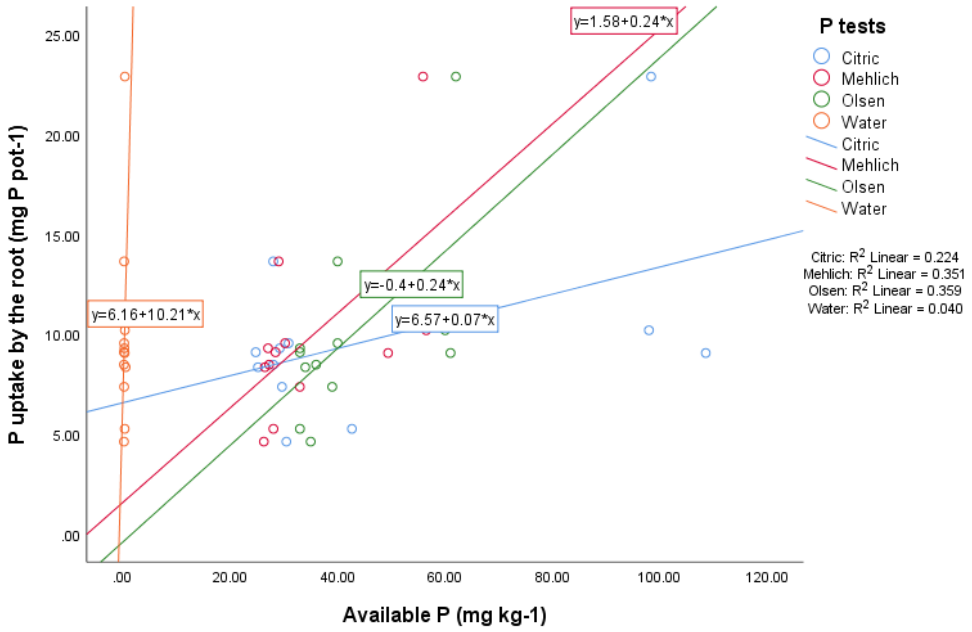


Figure S6.3. Relationship between the tall fescue dry mass shoots grown in soil A treated with different P sources (without biochar amendment) versus post-harvest available P (a) and total P (b) in the soil extracted by citric acid, and Mehlich-3 methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

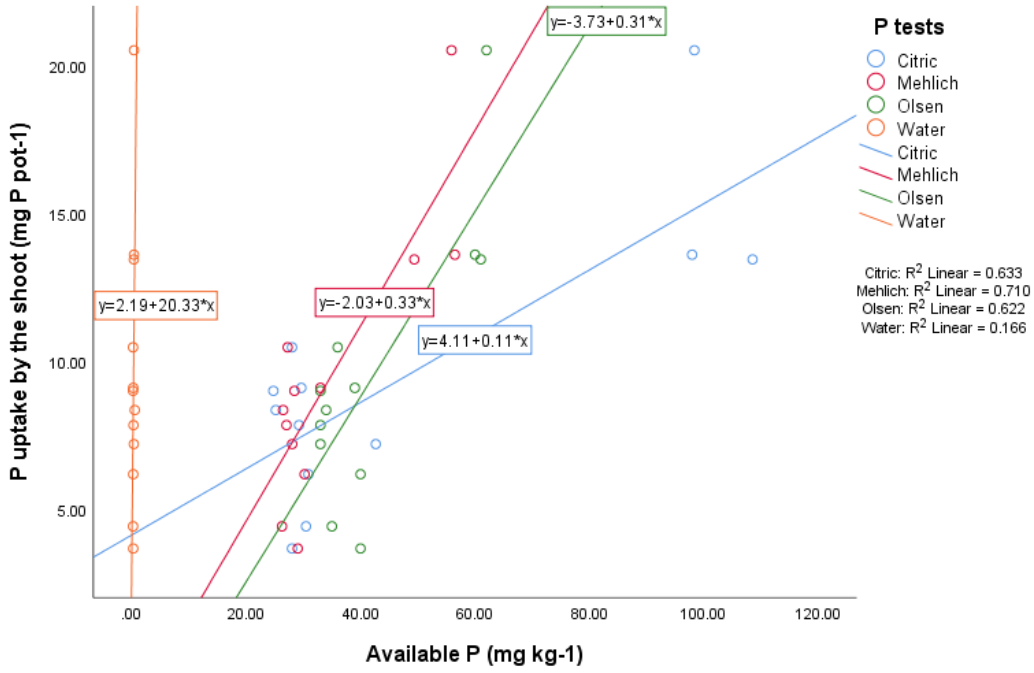
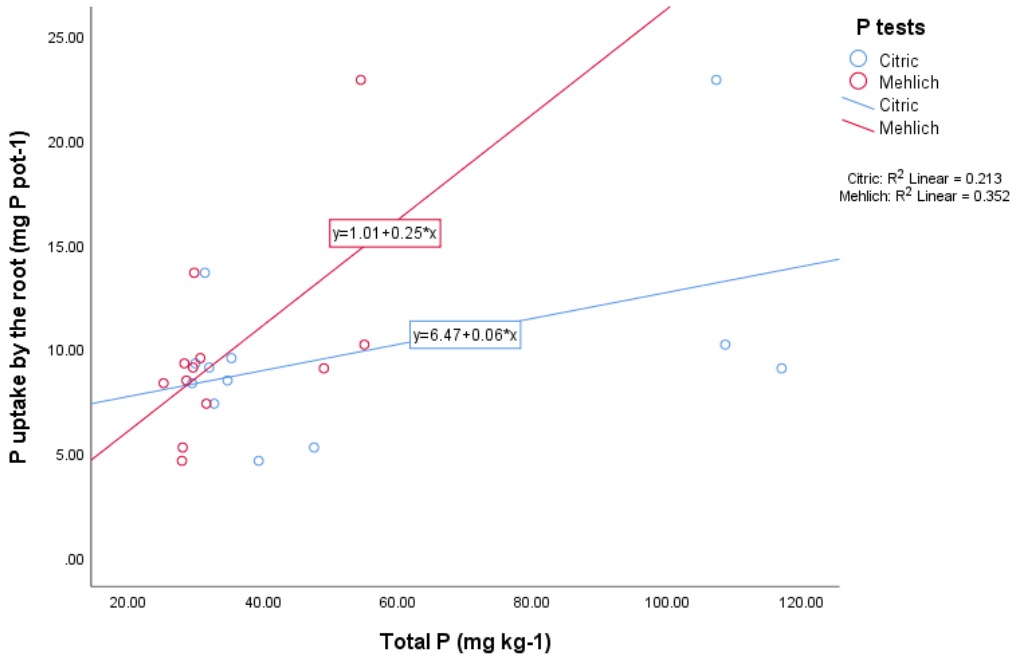


Figure S6.4. Relationship between P uptake by the tall fescue roots (a) and shoots(b) from soil A treated with different P sources (amended with biochar) versus post-harvest available P extracted by citric acid, Mehlich-3, Olsen, and water methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

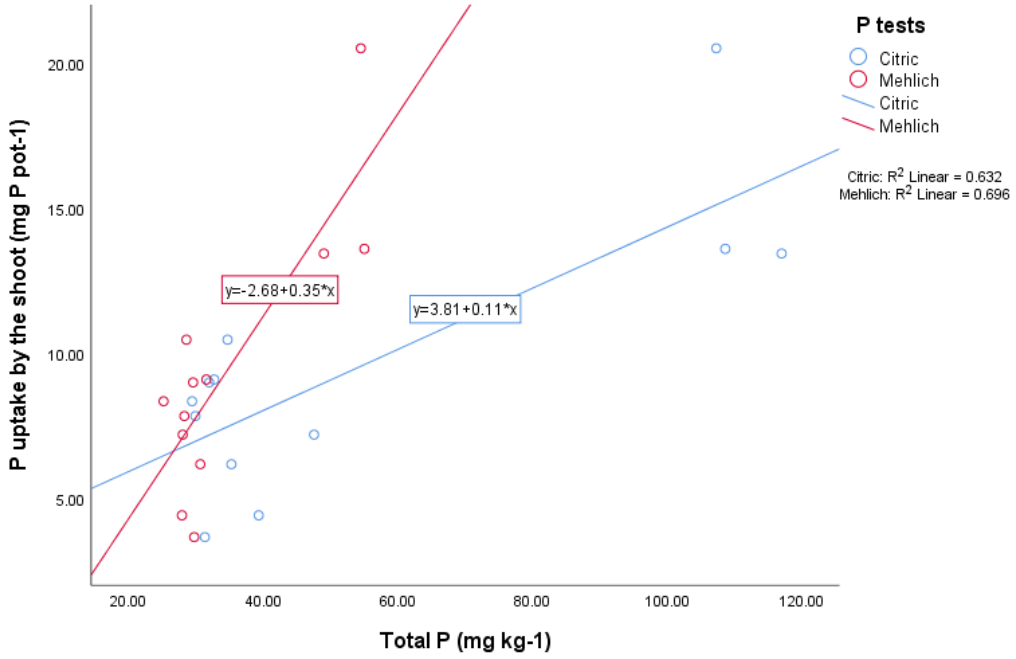
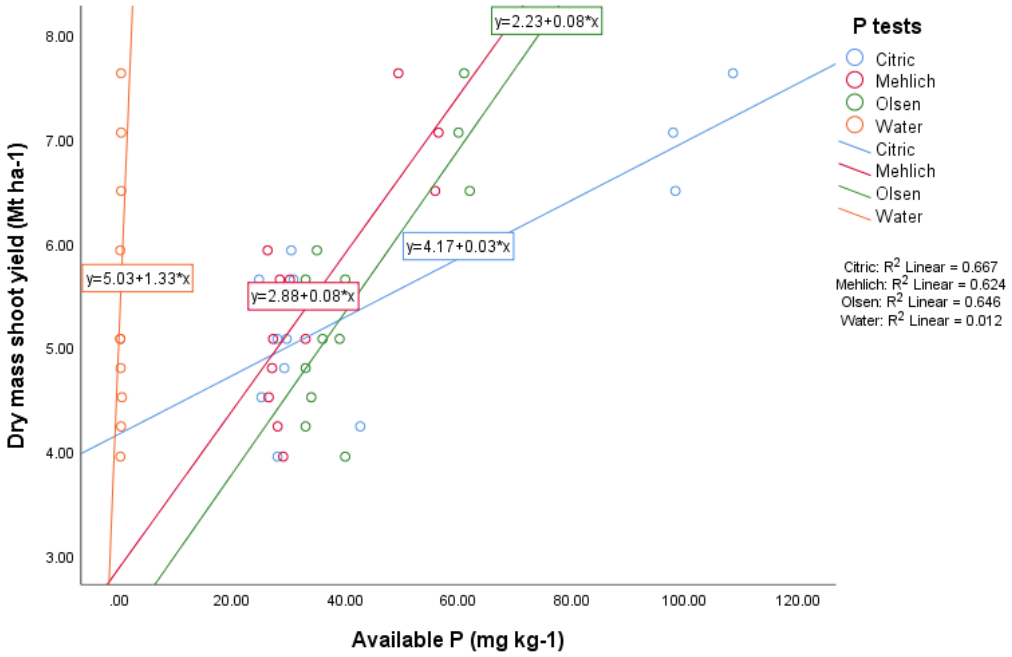


Figure S6.5. Relationship between P uptake by the tall fescue roots (a) and shoots(b) from soil A treated with different P sources (amended with biochar) versus post-harvest total P in the soil extracted by citric acid, and Mehlich-3 methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

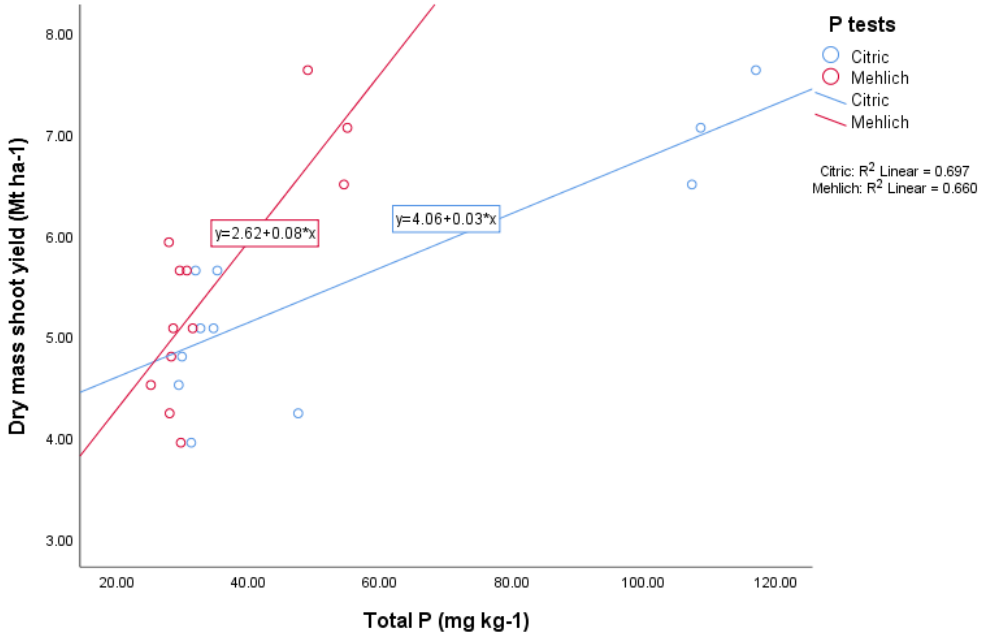
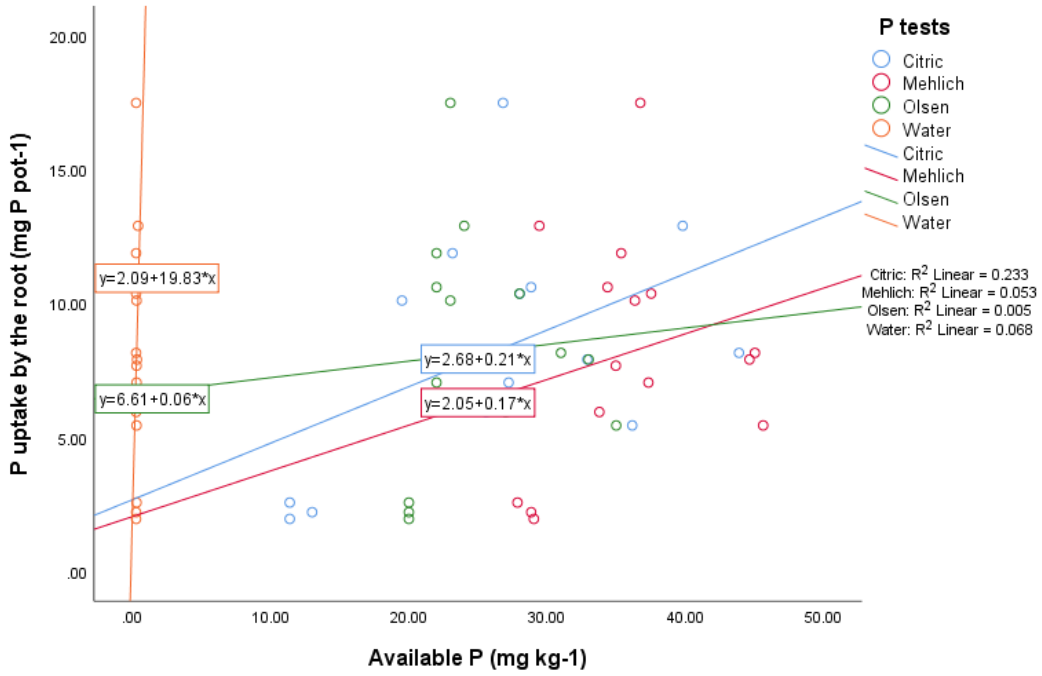


Figure S6.6. Relationship between the tall fescue dry mass shoots grown in soil A treated with different P sources (amended with biochar) versus post-harvest available P (a) and total P (b) in the soil extracted by citric acid, and Mehlich-3 methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

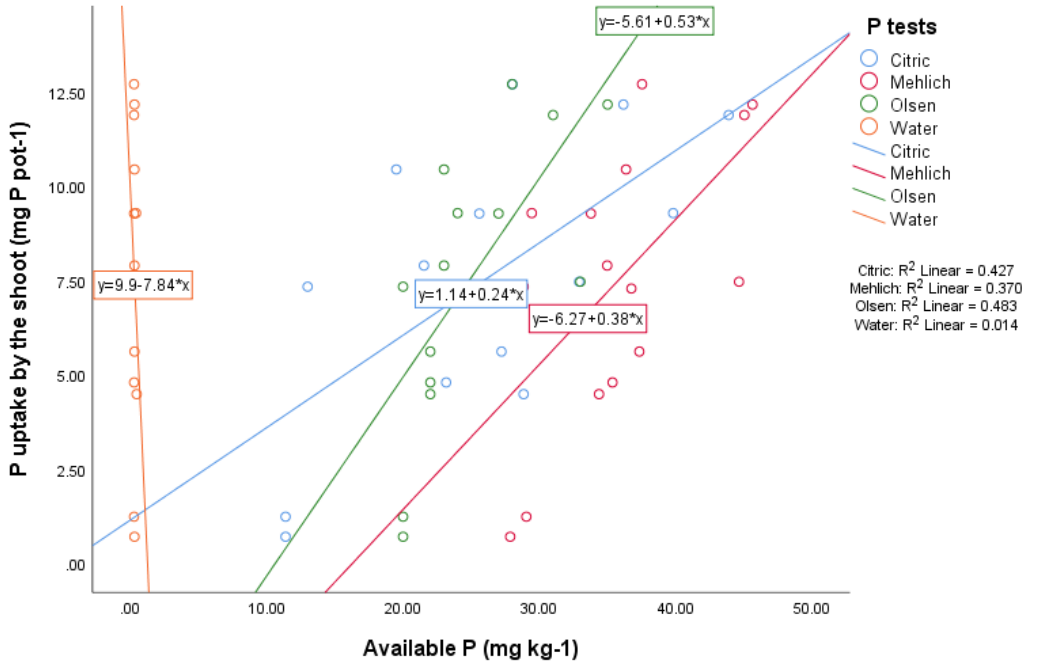
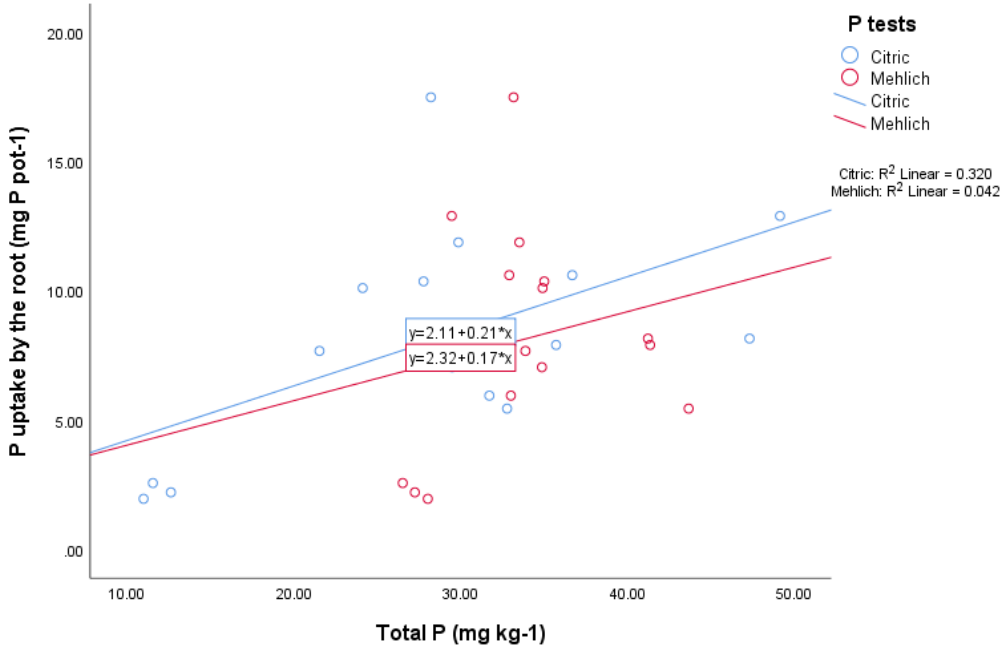


Figure S6.7. Relationship between P uptake by the tall fescue roots (a) and shoots(b) from soil B treated with different P sources (without biochar amendment) versus post-harvest available P in the soil extracted by citric acid, Mehlich-3, Olsen, and water methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

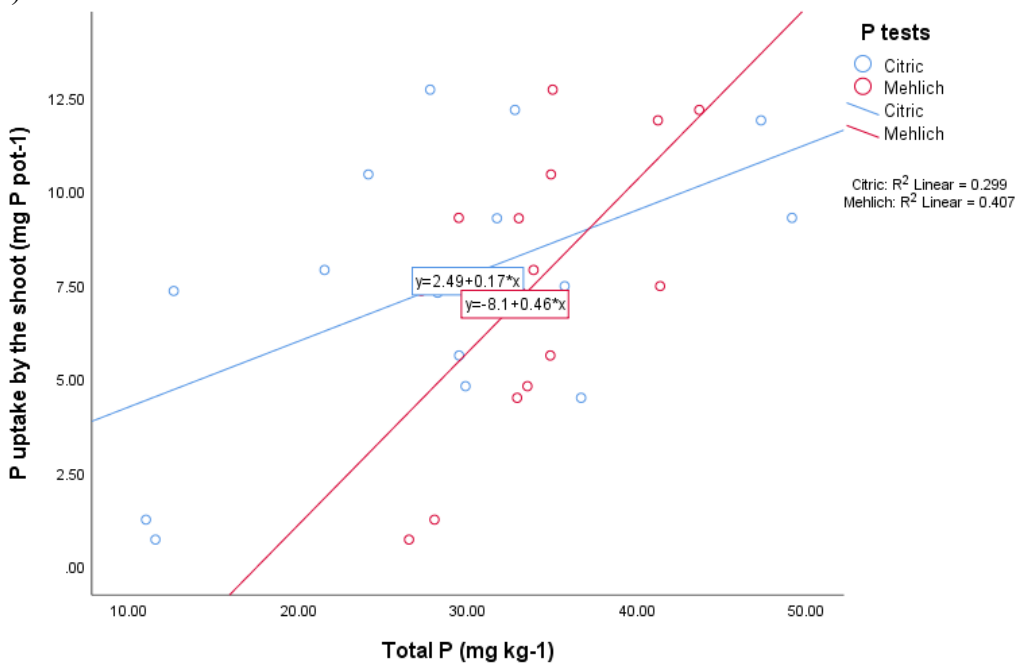
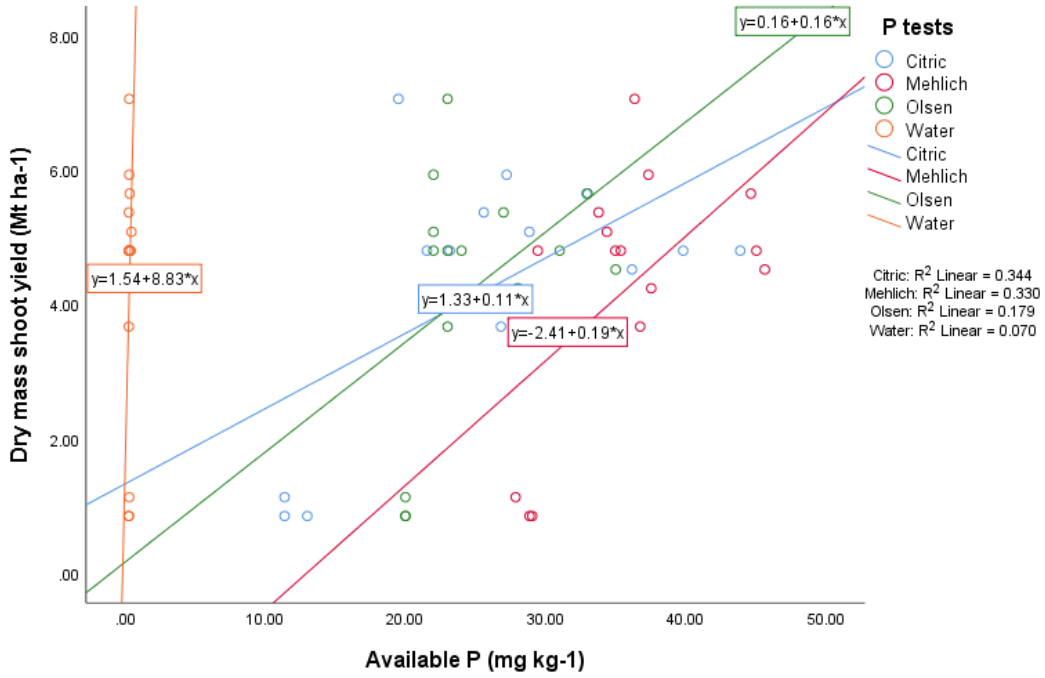


Figure S6.8. Relationship between P uptake by the tall fescue roots (a) and shoots (b) from soil B treated with different P sources (without biochar amendment) versus post-harvest total P in the soil extracted by citric acid and Mehlich-3 methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

(a)



(b)

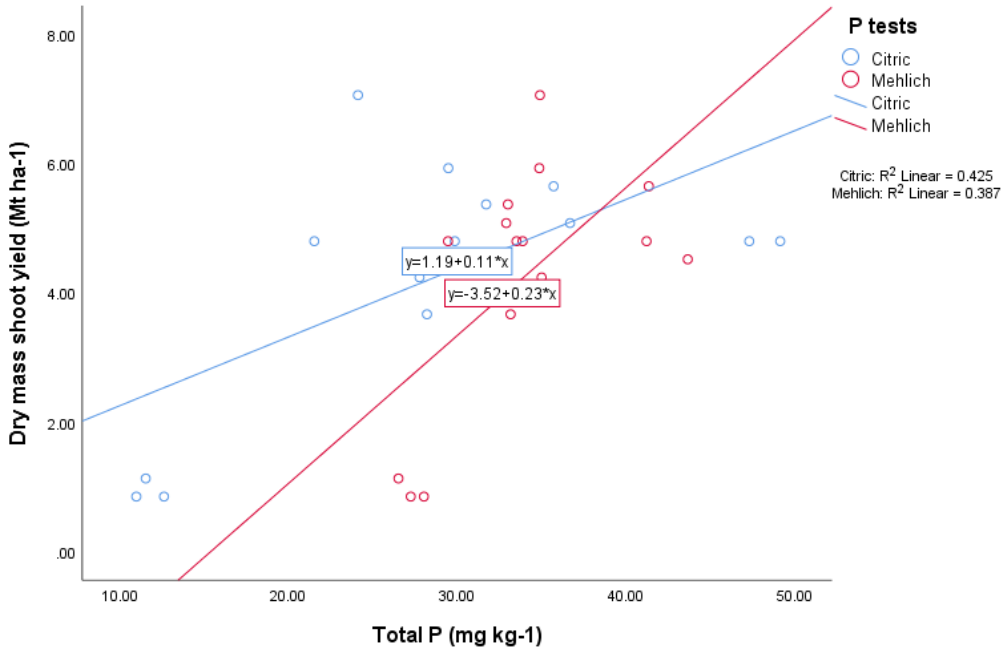


Figure S6.9. Relationship between the tall fescue dry mass shoots grown in soil B treated with different P sources (without biochar amendment) versus post-harvest available P (a) and total P (b) in the soil extracted by citric acid, and Mehlich-3 methods. Each point in the figure represents a replicate (pot), and their colour indicates the P extraction methods.

Chapter 7. SUMMARY AND CONCLUSION

To my knowledge this thesis is the first effort made to comprehend the P dynamics in the variably managed and distinct Nfld Podzols to support the development of sustainable P management in a small but expanding boreal agriculture industry with unique environmental conditions. The baseline farm soil test and the relationship between soil test and nutrient recommendations suggests a possible imbalance between P application and the soil's capacity to retain P. Overall, the baseline farm soil tests have shown that P in soils was crop dependent. Excessive application of P is likely mainly associated with dairy farms which led to higher soil P (greater than 200 mg P kg^{-1}, Mehlich-3 P) and P indexes. Also, the N recommendation is solely depending on crop type which might lead to excessive N application.

Ten agri-environmental P-*tests* employed to extract different P pools in variably managed Nfld soils. Mehlich-3, Olsen, and Bray-1 tests were able to extract significantly similar quantity of P in the Podzols soil while Bray-2 extracted significantly higher P from strongly fixed by minerals. Moreover 1% citric acid extracted significantly larger P pools in the Podzols soil. The correlation and linear regression confirmed that Mehlich-3 is the acceptable P-tests for Nfld agricultural Podzols. Nevertheless, Nfld managed and forested or natural soils have different P pools a fact pertinent for sustainable agri-environmental P management.

Furthermore, different P buffering capacity was observed in Podzols when assessed either by horizons, by depth, or by land-use. The newly converted or forested B and BC horizons serve as P sink while the Ap horizons of long-term managed podzolic soil could act as a

source and sink for P. Similarly, the surface (0-20 cm) long-term managed soils acted as source and sink for P while the subsurface (20-40 cm) soils act as a sink for P. P retention in natural and managed Podzols is likely due to both SOM and Al. Thus, future soil fertilisation research here and in similar scenarios across the boreal ecosystem must be carefully designed and interpreted to account for the variability in P kinetics.

Moreover, the P availability and uptake in Podzols recently converted from forest to agriculture were distinct between the surface (0-15 cm) layer and the immediate subsurface (15-30 cm) layer, with variable interactions between soil and P fertiliser sources. The relation between P-*tests* (Mehlich-3, Olsen, and 1% citric acid) and P uptake by roots and shoots and yield of tall fescue shoot was established based on the pot experiment.

In summary, despite the variability in the results related to the representativeness of the soil samples and limited farm soil testing information, this thesis has provided a deeper insight into the factors affecting P dynamics in terms of availability, species, mobility, and uptake in variably managed Nfld Podzols and offers a first insight into P chemistry (extractability and adsorption) on land-use converted Podzols. With a further understanding of detailed and complete P species, the impact of freezing and thawing, and the inclusion of more locations and management types, this study can be used as a platform to develop targeted interventions aimed at sustainable P management, for both economic and environmental advantages.